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EINSTEIN'S CONNECTIONS II

DEGENERATE CASES OF THE FIRST CLASS*

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ABSTRACT

In a recent paper (Lal and Mishra [3]), the solution of Einstein's first set of equations of the unified field theory has been studied in full details in holonomic and non-holonomic forms for the degenerate cases $g=0$, $D \neq 0$ of the first class for the indices of inertia 0 and 2 of $h_{\lambda\mu}$ in which cases only g can be zero ; and conditions for the existence of at least one solution in that case have been stated. The object of this paper is to give solutions of the said equation in holonomic form for the degenerate case $a^2 - 4\,kb^2 = 0$ of the first class when $D \neq 0$ and for the indices of inertia 0 and 4 of $h_{\lambda\mu}$ (in which cases only, $a^2 - 4\,kb^2$ can be zero) and to state conditions for the existence of at least one solution in each case.

1. *Introduction.* In Einstein's unified field theory the basic real tensor $g_{\lambda\mu}$ which has sixteen components is non-symmetric and may be split into its symmetric part $h_{\lambda\mu}$ and its skew symmetric part $k_{\lambda\mu}$:

(1.1)
$$g_{\lambda\mu} = h_{\lambda\mu} + k_{\lambda\mu}.$$

The tensor $h_{\lambda\mu}$ is assumed to be of rank 4 and to be of index of inertia 0 or 4 according as the signature of $h_{\lambda\mu}$ is $(++--)$ or $(++++)$ or any other equivalent combinations of $+$ and $-$ signs.

The basic connection $\Gamma^{\nu}_{\lambda\mu}$ is also non-symmetric and is given by

$$(1.2) \qquad D_{\omega} g_{\lambda\mu} = 2 \, S_{\omega\mu}^{\ \ \alpha} \, g_{\lambda\alpha} \, ,$$

Denoting by G, f, t the determinants of $g_{\lambda\mu}$, $h_{\lambda\mu}$ and $k_{\lambda\mu}$ and taking $h^{\lambda\mu}$ as a tensor inverse to $h_{\lambda\mu}$, let us put

$$(1.4)a \quad g \overset{def}{=} G/f$$

$$(1.4)b \quad k \overset{def}{=} t/f$$

$$(1.4)c \ \ (o) \ k^{\nu}_{\lambda} \overset{def}{=} \delta^{\nu}_{\lambda} \, ; \ (1) \ k^{\nu}_{\lambda} = k^{\nu}_{\lambda} \, ; \ (p) \ k^{\nu}_{\lambda} = (p-1) \ k^{\alpha}_{\lambda} \ k^{\nu}_{\alpha} \ (p = 2, 3, \ldots),$$

$$(1.4)d \quad 4K \overset{def}{=} k_{\alpha\beta} \ k^{\alpha\beta} = - (2) \ k^{\alpha}_{\alpha} \ .$$

We then have

$$(1.5) \qquad g = 1 + 2K + k.$$

The tensor $g_{\lambda\mu}$ or $k_{\lambda\mu}$ is said to be of the first class if $k \neq o$. For this class there are exactly four linearly independent vectors $\underset{i}{a^{\nu}}$ satisfying (Hlavaty [1] P 11)

$$(1.6) \qquad (a)_{x}^{\lambda} \underset{x}{a^{\mu}} = k^{\mu}_{\lambda} \underset{x}{a^{\lambda}} \quad (b) \ h_{\lambda\mu} \underset{x}{a^{\lambda}} \underset{x}{a^{\mu}} = 0,$$

where $\underset{x}{\lambda}$ are solutions of

$$(1.7) \qquad \lambda^{4} + 2K \lambda^{2} + k = 0.$$

The vectors $\underset{x}{a^{\nu}}$ are called eigen vectors of $k_{\lambda}^{\ \nu}$ and the scalars $\underset{x}{\lambda}$ are the corresponding eign-values.

Introduce a scalar D given by

(1.8) $D = K^2 - k,$

then for this class we have the basic scalars

(1.9)a $\alpha \overset{def}{=} \lambda_1 = -\lambda_2 = i \sqrt{\sqrt{D} + K} \neq 0$

(1.9)b $\beta \overset{def}{=} \lambda_3 = -\lambda_4 = \sqrt{\sqrt{D} - K} \neq 0,$

and the symmetric scalars λ_{ijk} given by

(1.10) $\lambda_{ijk} \overset{def}{=} 1 + \lambda_i \lambda_j + \lambda_j \lambda_k + \lambda_k \lambda_i$

are

(1.11)a $\lambda_{12i} = 1 + K + \sqrt{D}$

(1.11)b $\lambda_{34i} = 1 + K - \sqrt{D}$

(1.11)c $\lambda_{233} = \lambda_{144} = 1 - K - \sqrt{D} - 2\sqrt{k}$

(1.11)d $\lambda_{332} = \lambda_{441} = 1 - K + \sqrt{D} - 2\sqrt{k}$

(1.11)e $\lambda_{113} = \lambda_{224} = 1 - K - \sqrt{D} + 2\sqrt{k}$

(1.11)f $\lambda_{331} = \lambda_{442} = 1 - K + \sqrt{D} + 2\sqrt{k}$

It is easy to verify that

(1.12)a $(1 + K + \sqrt{D})(1 + K - \sqrt{D}) = g,$

and

(1.12)b $(i - K - \sqrt{D} - 2\sqrt{k})(1 - K + \sqrt{D} - 2\sqrt{k})(1 - K - \sqrt{D} + 2\sqrt{k})(1 - K + \sqrt{D} + 2\sqrt{k})$

$= (1 - 2K + 5k)^2 - 16k(1 - K)^2$

$= a^2 - 4k b^2$

where

(1.13) $a = 1 - 2K + 5k$ and $b = -2(1 - K)$

[3]

It has been shown by Hlavaty' ([1] PP. 52-53) that if the system (1·2) admits a solution $\Gamma^\nu_{\lambda\mu}$, it must be of the form

$$(1.14) \qquad \Gamma^\nu_{\lambda\mu} = \begin{Bmatrix} \nu \\ \lambda\mu \end{Bmatrix} + S_{\lambda\mu}{}^\nu + U^\nu{}_{\lambda\mu},$$

where $\begin{Bmatrix} \nu \\ \lambda\mu \end{Bmatrix}$ are the Christoffel symbols with respect to the tensor $h_{\alpha\beta}$ and

$$(1.15) \qquad U^\nu_{\lambda\mu} \overset{\text{def}}{=} 2h^{\nu\alpha} S_{\alpha(\lambda}{}^\beta k_{\mu)\beta}.$$

The tensors $S_{\lambda\mu}{}^\nu$ and $U^\nu_{\lambda\mu}$ are related by

$$(1.16) \qquad S_{\omega\mu\nu} = \tfrac{1}{2} K_{\omega\mu\nu} - 2 U_{\alpha\nu[\mu} k_{\omega]}{}^\alpha$$

where

$$(1.17) \qquad K_{\omega\mu\nu} \overset{\text{def}}{=} \nabla_\omega k_{\nu\mu} + \nabla_\mu k_{\omega\nu} + \nabla_\nu k_{\omega\mu},$$

the operator ∇_μ being the symbolic vector of the covariant derivative with respect to $\begin{Bmatrix} \nu \\ \lambda\mu \end{Bmatrix}$.

Since $U^\nu_{\lambda\mu}$ is symmetric in λ and μ, we have from (1.16)*,

$$(1.18) \qquad S_{[\omega\mu\nu]} = \tfrac{1}{2} K_{[\omega\mu\nu]}$$

Eliminating $U_{\omega\mu\nu}$ from (1.15) and (1.16) and using (1.18) we have

$$(1.19) \qquad S_{\omega\mu\nu} = \tfrac{1}{2}\left(K_{\omega\mu\nu} + 3k_\omega{}^\alpha k_\mu{}^\beta K_{[\alpha\beta\nu]} \right) - k_\omega{}^\alpha k_\mu{}^\beta S_{\alpha\beta\nu}$$
$$- k_\omega{}^\alpha k_\nu{}^\gamma S_{\alpha\mu\gamma} - k_\mu{}^\beta k_\nu{}^\gamma S_{\omega\beta\gamma}.$$

Also since $U^\nu_{\lambda\mu}$ is symmetric in λ and μ we have from (1.15),

$$(1.20)a \qquad U_{(\nu\lambda\mu)} = 0$$

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* Here we follow the notation

$${}_3T_{[\omega\mu\nu]} = T_{[\omega\mu]\nu} + T_{[\mu\nu]\omega} + T_{[\nu\omega]\mu} .$$

[4]

Eliminating $S_{\omega\mu\nu}$ from equations (1.15) and (1.16) and using (1.20)a we have

$(1.20)b \quad U_{\omega\mu\nu} = - k_{(\nu}{}^{\alpha} K_{\mu)\,\omega\,\alpha} - k_{\omega}{}^{\alpha} k_{\mu}{}^{\beta} U_{\alpha\beta\nu}$

$$- k_{\omega}{}^{\alpha} k_{\nu}{}^{\gamma} \cdot U_{\alpha\mu\gamma} - k_{\mu}{}^{\beta} k_{\nu}{}^{\gamma} U_{\omega\beta\gamma} \ .$$

If

$(1.21)a \qquad \overset{xyz}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma} \overset{def}{=} (x)\, k_{\omega}{}^{\alpha} \ (y)\, k_{\mu}{}^{\beta} \ (z)\, k_{\nu}{}^{\gamma},$

and

$(1.21)b \quad \overset{x_1 y_1 z_1}{A}{}_{\omega_1\mu_1\nu_1}^{\alpha\beta\gamma} \cdot \overset{x_2 y_2 z_2}{A}{}_{\omega_2\mu_2\nu_2}^{\omega_1\mu_1\nu_1} \cdots \overset{x_n y_n z_n}{A}{}_{\omega_n\ \mu_n\ \nu_n}^{\omega_{n-1}\ \mu_{n-1}\ \nu_{n-1}} = \overset{xyz}{A}{}_{\omega_n\mu_n\nu_n}^{\alpha\beta\gamma}$

$$(x = \textstyle\sum_n x_n \ , \quad y = \textstyle\sum y_n \ , \quad z = \textstyle\sum z_n)$$

and

$(1.21)e \quad 2\, \overset{(pq)r}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma} \overset{def}{=} \overset{pqr}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma} + \overset{qpr}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma},$

and

$(1.21)d \quad 3\, \overset{(pqr)}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma} \overset{def}{=} \overset{(pq)r}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma} + \overset{(qr)p}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma} + \overset{(rp)q}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma} \ ,$

then equation (1.19) can be put in the form

$(1.22)a \quad S_{\omega\mu\nu} = B_{\omega\mu\nu} - 3\, \overset{(110)}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma} S_{\alpha\beta\gamma}$

where

$(1.22)b \quad B_{\omega\mu\nu} = \tfrac{1}{2}\left(K_{\omega\mu\nu} + 3\, \overset{110}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma} K_{[\alpha\beta\gamma]}\right).$

If further T denotes the tensor $T_{\alpha\beta\gamma}$, and

$(1.23)a \quad \overset{pqr}{T} \overset{def}{=} \overset{pqr}{A} \times T \overset{def}{=} \overset{pqr}{A}{}_{\omega\mu\nu}^{\alpha\beta\gamma} T_{\alpha\beta\gamma}$

$(1.23)b \quad \overset{\circ\circ\circ}{T} \overset{def}{=} \overset{\circ\circ\circ}{A} \times T \overset{def}{=} T_{\omega\mu\nu}$

$(1.23)e \quad \overset{p_1 q_1 r_1}{B} \times \overset{p_2 q_2 r_2}{A} \overset{def}{=} \overset{p_1 q_1 r_1}{B}{}_{\omega\mu\nu}^{\alpha\beta\gamma} \cdot \overset{p_2 q_2 r_2}{A}{}_{\alpha\beta\gamma}^{\omega_1\mu_1\nu_1} \ ,$

then the equation (1.22)a assumes the form

$$(1.24) \qquad S = B - 3 \overset{(110)}{S}.$$

We have in the first class when $D \neq 0$

in the notation of (1.23), the following recurrence relations, (Mishra [2])

$$(1.25)a \qquad \overset{(32)r}{S} = k \overset{(10)r}{S}$$

$$(1.25)b \qquad \overset{(30)r}{S} = -2K \overset{(10)r}{S} - \overset{(12)r}{S}$$

$$(1.25)c \qquad 2 \overset{(13)r}{S} = k \overset{oor}{S} - 2K \overset{11r}{S} - \overset{22r}{S}$$

$$(1.25)d \qquad \overset{33r}{S} = k \overset{11r}{S} + 2K \overset{22r}{S} + 2k \overset{(20)r}{S}$$

We also have (Hlavaty [1] p. 23) in the first class when $D \neq 0$

$$(1.26)a \qquad {}^{(4)}k_\lambda^\nu + 2K\,{}^{(2)}k_\lambda^\nu + k\,\delta_\lambda^\nu = 0, \; k \neq 0.$$

From this we can easily prove

$$(1.26)b \qquad {}^{(p+4)}k_\lambda^\nu + 2K\,{}^{(p+2)}k_\lambda^\nu + k\,{}^{(p)}k_\lambda^\nu = 0, \quad p = 0, 1, 2, \ldots\ldots$$

Now using the relations (1.24) and (1.25) we have

in the first class when $D \neq 0$,

$$(1.27)a \qquad B = \overset{110}{S} + S + 2\overset{(10)1}{S},$$

$$(1.27)b \qquad \overset{(10)1}{B} = \overset{(10)1}{S} + \overset{(12)1}{S} + \overset{(20)2}{S} + \overset{112}{S},$$

$$(1.27)c \qquad 2\overset{(12)1}{B} = 2\overset{(12)1}{S} + 2k\overset{(10)1}{S} + k\overset{002}{S} - 2K\overset{112}{S} + \overset{222}{S},$$

$$(1.27)d \qquad 2\overset{(20)2}{B} = 2\overset{(20)2}{S} + k\overset{002}{S} - 2K\overset{112}{S} - 4K\overset{(10)3}{S} - \overset{222}{S},$$

$$(1.27)e \qquad \overset{(10)3}{B} = \overset{(10)3}{S} + \overset{(12)3}{S} - 2K\overset{(20)2}{S} - k\overset{(20)0}{S} - 2K\overset{112}{S} - k\overset{110}{S},$$

$$(1.27)f \qquad 2\overset{(12)3}{B} = 2\overset{(12)3}{S} + 2k\overset{(10)3}{S} - 2K\overset{002}{S} + 4K^2\overset{112}{S} - 2K\overset{222}{S} - k^2 S$$
$$+ 2Kk\overset{110}{S} - k\overset{220}{S},$$

$$(1.27)g \quad 2\,{}^{(20)0}B = 2\,{}^{(20)0}S + k\,S - 2K\,{}^{110}S - {}^{220}S - 4K\,{}^{(10)1}S,$$

$$(1.27)h \quad {}^{110}B = {}^{110}S + 2\,{}^{(12)1}S + {}^{220}S,$$

$$(1.27)i \quad {}^{112}B = {}^{112}S + 2\,{}^{(12)3}S + {}^{222}S,$$

$$(1.27)j \quad {}^{220}B = (1+2K)\,{}^{220}S + 2k\,{}^{(10)1}S + 2k\,{}^{(20)0}S + k\,{}^{110}S,$$

$$(1.27)k \quad {}^{222}B = (1+2K)\,{}^{222}S + k\,{}^{112}S + 2k\,{}^{(10)3}S + 2k\,{}^{(20)2}S,$$

$$(1.27)l \quad {}^{002}B = {}^{002}S + {}^{112}S + 2\,{}^{(10)3}S$$

By eliminating ${}^{(20)2}S$, ${}^{(12)1}S$, ${}^{(20)0}S$, ${}^{(10)3}S$, ${}^{112}S$, ${}^{220}S$, ${}^{(20)0}S$, ${}^{002}S$ and ${}^{222}S$ from equations (1·27) we get (Mishra [2] p. 883)

$$(1.28)a \quad B = S + 2\,{}^{(10)1}S + {}^{110}S,$$

$$(1.28)b \quad B_1 = -2kg(1+2K)\,{}^{(10)1}S + 2kg(1+K)\,{}^{110}S + 2g(1-2K)\,{}^{(12)3}S,$$

$$(1.28)c \quad B_2 = 2g(2K-1+k)\,{}^{(10)1}S - g(2K-1+2k)\,{}^{110}S + 4g\,{}^{(12)3}S,$$

$$(1.28)d \quad B_3 = 6kg\,{}^{(10)1}S + g(k-1)\,{}^{110}S + 2g\,{}^{(12)3}S,$$

where B_r ($r = 1, 2, 3$) stands for $B\omega\mu\nu_r$ and are given by

$$(1.28)e \quad B_1 = k^2 B + 2\,{}^{(12)3}B + 2Kk\,{}^{002}B + 2(k-2K^2)\,{}^{112}B - 2k\,{}^{(12)1}B$$
$$+ 2K\,{}^{222}B + 2k\,{}^{(20)2}B + 2k(1+2K+2K^2)\,{}^{110}B - 2k(1+2K)\,{}^{(10)3}B$$
$$- k(1+2K)\,{}^{220}B - 2k(1+2K)^2\,{}^{(10)1}B,$$

$$(1\cdot28)f \quad B_2 = 2(4K^2-1+k+4Kk)\,{}^{(10)1}B + 2(1+K)\,{}^{112}B - {}^{222}B - k\,{}^{002}B$$
$$+ 2\,{}^{(20)2}B + 4(K+k)\,{}^{(10)3}B + 2k\,{}^{(20)0}B - (4K^2-1+k+4Kk)\,{}^{110}B$$
$$- k^2 B + (2K-1+2k)\,{}^{220}B,$$

[7]

$$(1.28)g \quad \underset{3}{B} = 2k^2 B + 2\ {}^{(12)3}B - k\ {}^{002}B + 2K\ {}^{112}B + 2(1+2K)\ {}^{(12)1}B - {}^{222}B$$

$$+ 2k\ {}^{(10)3}B - (1+k)(1+2K)\ {}^{110}B + (1+k)\ {}^{220}B + 2k(1+2K)\ {}^{(10)1}B$$

$$- 2k\ {}^{(20)0}B,$$

Eliminating ${}^{(10)1}S$, ${}^{110}S$, ${}^{(12)3}S$ from equations (1.28) the solution of (1.19) in the first class when $D \neq 0$ is found to be

$$(1.29) \quad (S - B)g\,(a^2 - 4kb^2) = 4\ \underset{1}{B}\,(K - 1) + \underset{2}{B}\,(1 - 2K + 5k)$$

$$+ 2\ \underset{3}{B}\,(1 - 4K + 4K^2 - 5k).$$

From the form of the solution (1.29) it is clear that the necessary and sufficient conditions for the existence and uniqueness of the solution $S_{\omega\mu\nu}$ of (1.19) in the first class when $D \neq 0$, are

$$(1.30) \quad g\,(a^2 - 4kb^2) \neq 0.$$

If the non-holonomic components of $h_{\lambda\mu}$ and $h^{\lambda\mu}$ in the first class are given by

$$(1.31)a \qquad \left(h_{ij}\right) = \left(h^{ij}\right) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix},$$

then the non-holonomic components of $(p)\ k_\lambda{}^\nu$ and $(p)\ k_{\lambda\mu}$ are (Hlavaty[1] pp. 20-22)

$$(1.31)b \quad (p)\ \underset{x}{k}{}^{i} = \left(\underset{x}{\lambda}\right)^p \delta_x^i,$$

$$(1.31)c \quad (p)\,k_{xi} = \left(\underset{x}{\lambda}\right)^p h_{xi},$$

and the solution of (1.19) in the non-holonomic form is

(Hlavaty [1] p. 79)

$$(1.32)a \quad S_{xyz} = \frac{1}{2\underset{xyz}{\lambda}} \left(K_{xyz} + 3\,\underset{x}{\lambda}\,\underset{y}{\lambda}\,K_{[xyz]}\right)$$

with

$$(1.32)b \quad S_{[xyz]} = \tfrac{1}{2} K_{[xyz]}\ .$$

[8]

Since the non-holonomic components remain the same for all indices, solutions (1.32) ar e true for all indices of inertia.

From the form of the solution (1.32)a in non-holonomic form it is clear that the necessary and sufficient conditions for the existence and uniqueness of the solution $S_{\omega\mu\nu}$ of (1.19) in the first class when $D \neq 0$, are

(1.33) $\qquad \lambda_{ijk} \neq 0$ for all i, j, k

which by using (1.11) is equivalent to

(1.34) $\qquad (1 + K + \sqrt{D})\, (1 + K - \sqrt{D})\, (1 - K - \sqrt{D} - 2\sqrt{k})\, (1 - K$
$\qquad + \sqrt{D} - 2\sqrt{k})\, (1 - K - \sqrt{D} + 2\sqrt{k})\, (1 - K + \sqrt{D}\ 2\sqrt{k}) \neq 0,$

and by virtue of (1.12) and (1.13), the condition (1.34) reduces to

(1.35) $\qquad g\, (a^2 - 4\, k\, b^2) \neq 0 \qquad$.

the same as (1.30).

2. *Degenerate cases of the first class when* $D \neq 0$.

(*a*) When the index of inertia of $h_{\lambda\mu}$ is zero, the determinant f of $h_{\lambda\mu}$ is positive and as k is non-negative always, $k = \dfrac{t}{f} \geqslant 0$. Consequently for the first class when the index of inertia is zero, $k > 0$ and hence $a^2 - 4\, k\, b^2$ may be zero. Further since K can be negative in this case, g may also be zero. Hence the necessary and sufficient condition for the existence and uniqueness of the solution of (1.29) in the first class when $D \neq 0$ is

(2.1)$a \qquad g\, (a^2 - 4\, k\, b^2) \neq 0.$

Whereas if we consider the solution in the non-holonomic form, as given by (1.32)a the necessary and sufficient conditions for the existence and uniqueness of the solution $S_{\omega\mu\nu}$ of (1.19) in the first class for the index of inertia zero, when $D \neq 0$,

are

(2.1)$b \qquad \lambda_{ijk} \neq 0$ for all indices i, j, k which by using (1.11) is equiva lent to

(2.1)$c \qquad (1 + K + \sqrt{D})\, (1 + K - \sqrt{D})\, (1 - K - \sqrt{D} - 2\sqrt{k})\, (1 - K + \sqrt{D}$
$\qquad - 2\sqrt{k})\, (1 - K - \sqrt{D} + 2\sqrt{k})\, (1 - K + \sqrt{D} + 2\sqrt{k}) \neq 0 \cdot$

It may be noted that if $D > 0$, (2.1)c holds as a necessary and sufficient condition for the existence and uniqueness of the solution. But if $D < 0$, then since $k > 0$, each of the factors in (2.1)c is complex and hence not zero *i.e.* the condition (2.1)c in this case is automatically satisfied.

[9]

(b) When the index of inertia of $h_{\lambda\mu}$ is 2, the determinant f of $h_{\lambda\mu}$ is negative and hence $k < 0$ and $D > 0$. For this reason $a^2 - 4k b^2$ is always positive. Thus the condition (1.30) reduces to

(2.2)a $\qquad g \neq 0$

In the non-holonomic from, the condition (1.33) for this case reduces to

(2.2)b $\qquad \overset{\lambda}{12i} \cdot \overset{\lambda}{34j} \neq 0,$

or

(2.2)c $\qquad (1 + K + \sqrt{D})(1 + K - \sqrt{D}) \neq 0,$

since, k being negative, other $\overset{\lambda}{ijk}$ are complex and hence not zero.

(c) When the index of inertia of $h_{\lambda\mu}$ is 4, the determinant f of $h_{\lambda\mu}$ is positive and hence $k > 0$, for the first class. Also since index of inertia is 4, K can be considered as the sum of four squares, and thus $K > 0$. Further since $g = 1 + 2K + k$, $g > 0$. Hence the condition (1.30) when $D \neq 0$ reduces to

(2.3)a $\qquad a^2 - 4 k b^2 \neq 0.$

In the non-holonomic form the condition (1.33) reduces to

(2.3)b $\qquad (1 - K - \sqrt{D} - 2\sqrt{k})(1 - K + \sqrt{D} - 2\sqrt{k})(1 - K - \sqrt{D}$
$\qquad\qquad\qquad - 2\sqrt{k})(1 - K + \sqrt{D} - 2\sqrt{k}) \neq 0.$

The reason why two factors $1 + K + \sqrt{D}$ and $1 + K - \sqrt{D}$ are omitted is because g is greater than zero in this case.

It may be noted in this case again that if $D > 0$, (2.3)b holds as a necessary and sufficient condition for the existence and uniqueness of the solution since $k > 0$. But if $D < 0$, each of the factors in (2.3)b is complex and hence not zero i.e. condition (2.3)b in this case is automatically satified.

Thus inequalities (2.1)a (2.2)a and (2.3)a suggest that if we consider the solution $S_{\omega\mu\nu}$ of (1.19) in the first class when $D \neq 0$, in holonomic form, there are two singular cases

(2.4) $g = 0$ when index of inertia is 0 or 2

and

(2.5) $\qquad a^2 - 4 k b^2 = 0$ when index of inertia is 0 or 4.

Whereas inequalities (2.1)c, (2.2)c and (2.3)b suggest that if we consider the solution in non-holonomic form, there are six singular cases, out of which two are

(2.6) $\qquad \overset{\lambda}{12i} = 0$

(2.7) $\qquad \overset{\lambda}{34i} = 0$ $\qquad$ when index of inertia is 0 or 2, corresponding to the case

(2.4) (Already done fully in Lal and Mishra [3]), and the other four cases are

(2.8) $\quad 1 - K - \sqrt{D} - 2\sqrt{k} = 0$
(2.9) $\quad 1 - K + \sqrt{D} - 2\sqrt{k} = 0$
(2.10) $\quad 1 - K - \sqrt{D} + 2\sqrt{k} = 0$ when the index of inertia is 0 or 4,
(2.11) $\quad 1 - K + \sqrt{D} + 2\sqrt{k} = 0$

corresponding to the case (2.5) which is proposed to be considered in this paper.

I shall now show that the conditions for the existence of at least one solution $S_{\omega\mu\nu}$ of (1.19) in the first class when $D \neq 0$ for the case $a^2 - 4 k b^2$ by considering the solution in holonomic form as obtained by the method of repeated substitution include the conditions for the existence of at least one solution $S_{\omega\mu\nu}$ of (1.19) in the first class when $D \neq 0$ for all four cases (2.8), (2.9), (2.10) and (2.11) as obtained by considering the solution in non-holonomic form. The solution $S_{\alpha\mu\nu}$ of (1.19) in the first class when $D \neq 0$ for the case $a^2 - 4 k b^2 = 0$ shall also be given in holonomic form. The solution $U_{\omega\mu\nu}$ of (1.20)b for the same case shall also be considered.

3. *Singular Solutions*: $D \neq 0$ and $1 - K - \sqrt{D} - 2\sqrt{k} = 0$.

Lemma (3.1). *In the first class when $D \neq 0$ and $1 - K - \sqrt{D} - 2\sqrt{k} = 0$ the basic scalars are given by*

(3.1)a $\qquad \alpha \overset{def}{=} \underset{1}{\lambda} = - \underset{2}{\lambda} = \sqrt{2\sqrt{k} - 1}$,

(3.1)b $\qquad \beta \overset{def}{=} \underset{3}{\lambda} = - \underset{4}{\lambda} = \sqrt{1 - 2K - 2\sqrt{k}}$,

and the symmetric scalars $\underset{ijk}{\lambda}$ *are given by*

(3.2)a $\qquad \underset{12i}{\lambda} = 2(1 - \sqrt{k})$,

(3.2)b $\qquad \underset{34i}{\lambda} = 2(K + \sqrt{k})$,

(3.2)c $\qquad \underset{ajf}{\lambda} = 2(1 - K - \sqrt{k} + (-1)^{a+j}\sqrt{k})$,

(3.2)d $\qquad \underset{aaf}{\lambda} = 4\sqrt{k}$ when $a + f$ is even,

(3.2)f $\qquad \underset{aaf}{\lambda} = 0$ when $a + f$ is odd.

PROOF. The equations (3.1) follows at once from (1.9) when $1 - K - 2\sqrt{k}$ is substituted for $\sqrt{D}$ in it. The equations (3.2) follows immediately from (1.11) and (3.1).

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THEOREM (3.1). *A necessary and sufficient condition that the equations* (1.19) *admit at least one solution S when* $D \neq 0$ *and* $1 - K - \sqrt{D} - 2\sqrt{k} = 0$, *is*

(3.3) $\mathrm{K}_{faa} = 0$, $a + f$ **is odd.**

PROOF. Substituting $\overset{\lambda}{\underset{ijk}{}}$ from (3.2) in the equation (1.32)a, it is obvious that the condition required is (3.3).

THEOREM (3.2) *When the condition* (3.3) *is satisfied, the solution* $\mathrm{S}_{\omega\mu\nu}$ *of* (*1.19*) *in the first class when* $\mathrm{D} \neq 0$, *and* $1 - K - \sqrt{D} - 2\sqrt{k} = 0$ *has non-holonomic components in the form* : ($a \neq b$, $e \neq f$),

(3.4)a the components S_{faa} are arbitrary

  when $a + f$ is odd,

(3.4)b $S_{faa} = \dfrac{1}{2\underset{faa}{\lambda}}\,\mathrm{K}_{faa}$, $a+f$ is even,

(3.4)c $S_{efg} = \dfrac{1}{2\underset{efg}{\lambda}}\,\mathrm{K}_{efg}$,

(3.4)d $S_{efa} = \dfrac{1}{2\underset{efa}{\lambda}}\Big(\mathrm{K}_{efa} + 3\,\overset{\lambda}{e}\,\overset{\lambda}{f}\,\mathrm{K}_{[efa]}\Big)$,

(3.4)e $S_{aef} = \dfrac{1}{2\underset{aef}{\lambda}}\Big(\mathrm{K}_{aef} + 3\,\overset{\lambda}{a}\,\overset{\lambda}{e}\,\mathrm{K}_{[aef]}\Big)$,

(3.4)f $S_{abc} = \dfrac{1}{2\underset{abc}{\lambda}}\mathrm{K}_{abc}$,

(3.4)g $S_{abf} = \dfrac{1}{2\underset{abf}{\lambda}}\Big(\mathrm{K}_{abf} + 3\,\overset{\lambda}{a}\,\overset{\lambda}{b}\,\mathrm{K}_{[abf]}\Big)$,

(3.4)h $S_{fab} = \dfrac{1}{2\underset{fab}{\lambda}}\Big(\mathrm{K}_{fab} + 3\,\overset{\lambda}{f}\,\overset{\lambda}{a}\mathrm{K}_{[fab]}\Big)$,

(3.4)i $S_{aff} = \dfrac{1}{2\underset{aff}{\lambda}}\,\mathrm{K}_{aff}$,

where λ's *are to be taken from (3.1) and (3.2).*

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PROOF. Writing (1.19) in the non-holonomic form and using (3.1) and (3.2), we obtain (3.4), the non-holonomic components S_{ijk} of $S_{\alpha\mu\nu}$.

4. Singular Solutions : $D \neq 0$ and $1 - K + \sqrt{D} - 2\sqrt{k} = 0$

Lemma (4.1). *In the first class when* $D \neq 0$ *and* $1 - K + \sqrt{D} - 2\sqrt{k} = 0$ *the basic scalars are given by*

$$(4.1)a \qquad \alpha \overset{def}{=} \overset{\lambda}{1} = -\overset{\lambda}{2} = \sqrt{1 - 2K - 2\sqrt{k}},$$

$$(4.1)b \qquad \beta \overset{def}{=} \overset{\lambda}{3} = -\overset{\lambda}{4} = \sqrt{2\sqrt{k} - 1},$$

and the symmetric scalars $\overset{\lambda}{ijk}$ *are given by*

$$(4.2)a \qquad \overset{\lambda}{12i} = 2(K + \sqrt{k}),$$

$$(4.2)b \qquad \overset{\lambda}{34i} = 2(1 - \sqrt{k}),$$

$$(4.2)c \qquad \overset{\lambda}{aff} = 4\sqrt{k} \qquad a + f \text{ is even},$$

$$(4.2)d \qquad \overset{\lambda}{aff} = 0 \qquad a + f \text{ is odd},$$

$$(4.2)e \qquad \overset{\lambda}{aaf} = 2(1 - K - \sqrt{k} + \varepsilon\sqrt{k}),$$

$$\text{where } \varepsilon = (-1)^{a+f}.$$

PROOF. The equations (4.1) follow at once from (1.9) when $2\sqrt{k} + K - 1$ is substituted for $\sqrt{D}$ in it. The equations (4.2) follow immediately from (1.11) and (4.1).

THEOREM (4.1). *A necessary and sufficient condition that the equations (1.19) admit at least one solution S when* $D \neq 0$ *and* $1 - K + \sqrt{D} - 2\sqrt{k} = 0$ *is*

$$(4.3) \qquad K_{aff} = 0, \qquad a + f \text{ is odd}.$$

PROOF. Substituting $\overset{\lambda}{ijk}$ from (4.2) in the equation (1.32)a it is obvious that the condition required is (4.3).

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THEOREM (4.2). *When the condition (4.3) is satisfied the solution* $S_{\omega\mu\nu}$ *of (1.19) in the first class when* $D \neq 0$ *and* $I - K + \sqrt{D} - 2\sqrt{k} = 0$ *has non-holonomic components in the form :* $(a \neq b, e \neq f)$,

$(4.4)a$ the components S_{aff} are arbitrary

when $a + f$ is odd,

$(4.4)b$ $\underset{aff}{S_{aff}} = \dfrac{1}{2\lambda} \underset{aff}{K_{aff}}, \quad a + f$ is even,

$(4.4)c$ $\underset{efg}{S_{efg}} = \dfrac{1}{2\lambda} \underset{efg}{K_{efg}}$,

$(4.4)d$ $\underset{efa}{S_{efa}} = \dfrac{1}{2\lambda}\left(\underset{efa}{K_{efa}} + 3 \underset{e}{\lambda}\underset{f}{\lambda} K_{[efa]} \right)$,

$(4.4)e$ $\underset{aef}{S_{aef}} = \dfrac{1}{2\lambda}\left(\underset{aef}{K_{aef}} + 3 \underset{a}{\lambda}\underset{e}{\lambda} K_{[aef]} \right)$,

$(4.4)f$ $\underset{abc}{S_{abc}} = \dfrac{1}{2\lambda} \underset{abc}{K_{abc}}$;

$(4.4)g$ $\underset{abf}{S_{abf}} = \dfrac{1}{2\lambda}\left(K_{abf} + 3 \underset{a}{\lambda}\underset{b}{\lambda} K_{[abf]} \right)$,

$(4.4)h$ $\underset{fab}{S_{fab}} = \dfrac{1}{2\lambda}\left(\underset{fab}{K_{fab}} + 3 \underset{f}{\lambda}\underset{a}{\lambda} K_{[fab]} \right)$,

$(4.4)i$ $\underset{faa}{S_{faa}} = \dfrac{1}{2\lambda} \underset{faa}{K_{faa}}$,

where λ's *are to be taken from (4.1) and (4.2).*

PROOF. Writing (1.19) in the non-holonomic form and using (4.1) and (4.2), we obtain (4.4) the non-holonomic components S_{ijk} of $S_{\omega\mu\nu}$.

5. Singular Solution : $D \neq 0$ and $1 - K - \sqrt{D} + 2\sqrt{k} = 0.$

Lemma (5.1). *In the first class when $D \neq 0$ and $1 - K - \sqrt{D} + 2\sqrt{k} = 0$, the basic scalars are given by*

$$(5\cdot1)a \qquad \alpha \overset{\text{def}}{=} \underset{1}{\lambda} = - \underset{2}{\lambda} = \sqrt{-1 - 2\sqrt{k}} \, ,$$

$$(5.1)b \qquad \beta \overset{\text{def}}{=} \underset{3}{\lambda} = - \underset{4}{\lambda} = \sqrt{1 - 2K + 2\sqrt{k}} \, ,$$

and the symmetric scalars $\underset{ijk}{\lambda}$ are given by

$$(5.2)a \qquad \underset{12i}{\lambda} = 2(1 + \sqrt{k}),$$

$$(3.2)b \qquad \underset{34i}{\lambda} = 2(K - \sqrt{k}),$$

$$(5.2)c \qquad \underset{aff}{\lambda} = 2(1 - K + \sqrt{k} + (-1)^{a+f}\sqrt{k}),$$

$$(5.2)d \qquad \underset{aaf}{\lambda} = -4\sqrt{k} \qquad a + f \text{ is odd,}$$

$$(5.2)e \qquad \underset{aaf}{\lambda} = 0, \qquad a + f \text{ is even.}$$

PROOF. The equations $(5\cdot1)$ follow at once from $(1\cdot9)$ when $1 - K + 2\sqrt{k}$ is substituted for $\sqrt{D}$ in it. The equations (5.2) follow immediately from (1.11) and (5.1).

THEOREM (5.1). *A necessary and sufficient condition that the equations (1.19) admit at least one solution S when $D \neq 0$, $1 - K - \sqrt{D} + 2\sqrt{k} = 0$ is*

$$(5.3) \qquad K_{faa} = 0, \quad a + f \text{ is even.}$$

PROOF. Substituting $\underset{ijk}{\lambda}$ from (5.2) in the equation $(1.32)a$ it is obvious that the condition required is (5.3).

THEOREM (5.2). *When the condition (5.3) is satisfied the solution $S_{\omega\mu\nu}$ of (1.19) in the first class when $D \neq 0$ and $1 - K - \sqrt{D} + 2\sqrt{k} = 0$ has non-holonomic components in the form : $(a \neq b, e \neq f)$,*

$(5.4)a$ the components S_{faa} are arbitrary
    when $a + f$ is even,

$$(5.4)b \qquad S_{faa} = \frac{1}{2\underset{faa}{\lambda}} K_{faa}, \quad a + f \text{ is odd,}$$

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$(5.4)c \quad \underset{efg}{S_{efg}} = \frac{1}{2\lambda} K_{efg},$

$(5.4)d \quad \underset{efa}{S_{efa}} = \frac{1}{2\lambda}\left(K_{efa} + 3 \underset{e}{\lambda}\underset{f}{\lambda} K_{[efa]}\right),$

$(5.4)e \quad \underset{aef}{S_{aef}} = \frac{1}{2\lambda}\left(K_{aef} + 3 \underset{a}{\lambda}\underset{e}{\lambda} K_{[aef]}\right),$

$(5.4)f \quad \underset{abc}{S_{abc}} = \frac{1}{2\lambda} K_{abc},$

$(5.4)g \quad \underset{abf}{S_{abf}} = \frac{1}{2\lambda}\left(K_{abf} + 3 \underset{a}{\lambda}\underset{b}{\lambda} K_{[abf]}\right),$

$(5.4)h \quad \underset{fab}{S_{fab}} = \frac{1}{2\lambda}\left(K_{fab} + 3 \underset{f}{\lambda}\underset{a}{\lambda} K_{[fab]}\right),$

$(5.4)i \quad \underset{aff}{S_{aff}} = \frac{1}{2\lambda} K_{aff},$

where λ's are to be taken from (5.1) and (5.2)

PROOF. Writing (1.19) in the non-holonomic form and using (5.1) and (5.2), we obtain (5·4), the non-holonomic components S_{ijk} of $S_{\omega\mu\nu}$.

6. *Singular Solutions : $D \neq 0$ and $1 - K - \sqrt{D} + 2\sqrt{k} = 0$*

Lemma (6.1). *In the first class when $D \neq 0$ and $1 - K + \sqrt{D} + 2\sqrt{k} = 0$ the basic scalars are given by*

$(6.1)a \quad \alpha \overset{\text{def}}{=} \underset{1}{\lambda} = -\underset{2}{\lambda} = \sqrt{1 + 2\sqrt{k} - 2K},$

$(6.1)b \quad \beta \overset{\text{def}}{=} \underset{3}{\lambda} = -\underset{4}{\lambda} = \sqrt{-1 - 2\sqrt{k}},$

and the symmetric scalars $\underset{ijk}{\lambda}$ are given by

$(6.2)a \quad \underset{12i}{\lambda} = 2(K - \sqrt{k}),$

$(6.2)b \quad \underset{34i}{\lambda} = 2(1 + \sqrt{k}),$

$(6.2)c \quad \underset{a f f}{\lambda} = 0 \quad , \qquad a + f$ is even,

$(6.2)d \quad \underset{a f f}{\lambda} = - 4 \sqrt{k}, \qquad a + f$ is odd,

$(6.2)e \quad \underset{a a f}{\lambda} = 2 (1 - K + \sqrt{k} + (-1)^{a+f} \sqrt{k}).$

Proof. The equations (6.1) follow at once from (1.9) when $K - 1 - 2 \sqrt{k}$ is substituted for $\sqrt{D}$ in it. The equations (6.2) follow immediately from (1.11) and (6.1).

THEOREM (6.1). *A necessary and sufficient condition that the eqations (1.19) admit at least one solution S when $D \neq 0$ and $1 - K + \sqrt{D} + 2 \sqrt{k} = 0$ is*

$(6.3) \quad \underset{a f f}{K} = 0 , \qquad a + f$ is even.

PROOF. Substituting $\underset{i j k}{\lambda}$ from (6.2) in the equation (1.32)a it is obvious that the condition required is (6.3).

THEOREM (6.2). *When the condition (6.3) is satisfied, the solution $S_{\omega \mu \nu}$ of (1.19) in the first class when $D \neq 0$, and $1 - K + \sqrt{D} + 2 \sqrt{k} = 0$ has non-holonomic components in the form :- ($a \neq b, e \neq f$).*

$(6.4)a \qquad$ the components $S_{a f f}$ are arbitrary

$\qquad$ when $a + f$ is even,

$(6.4)b \qquad S_{a f f} = \dfrac{1}{2 \underset{a f f}{\lambda}} \underset{a f f}{K}, \, a + f$ is odd,

$(6.4)c \qquad S_{e f g} = \dfrac{1}{2 \underset{e f g}{\lambda}} \underset{e f g}{K},$

$(6.4)d \qquad S_{e f a} = \dfrac{1}{2 \underset{e f a}{\lambda}} \left(\underset{e f a}{K} + 3 \underset{e}{\lambda} \underset{f}{\lambda} K_{[e f a]} \right),$

$(6.4)e \qquad S_{a e f} = \dfrac{1}{2 \underset{a e f}{\lambda}} \left(\underset{a e f}{K} + 3 \underset{a}{\lambda} \underset{e}{\lambda} K_{[a e f]} \right),$

$(6.4)f \qquad S_{a b c} = \dfrac{1}{2 \underset{a b c}{\lambda}} \underset{a b c}{K}$

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$$(\overset{\circ}{6.4})g \quad S_{abf} \underset{abf}{=} \frac{1}{2\lambda}\left(K_{abf} + 3\overset{\lambda}{a}\overset{\lambda}{b}K_{[abf]}\right).$$

$$(6.4)h \quad S_{fab} \underset{fab}{=} -\frac{1}{2\lambda}\left(K_{fab} + 3\overset{\lambda}{f}\overset{\lambda}{a}K_{[fab]}\right),$$

$$(6.4)i \quad S_{faa} \underset{faa}{=} -\frac{1}{2\lambda}K_{faa}.$$

where λ's are to be taken from (6.1) and (6.2).

PROOF. Writing (1.19) in the non-holonomic form and using (6.1) and (6·2), we obtain (6.4) the non-holonomic components S_{ijk} of $S_{\omega\mu\nu}$.

7. Existence Theorem : $D \neq 0$, and $a^2 - 4kb^2 = 0$.

THEOREM (7.1). *A necessary and sufficient condition that the equations (1.27) admit at least one solution S when* $D \neq 0$ *and* $a^2 - 4kb^2 = 0$ *is*

$$(7.1) \qquad \left(\overset{p}{0} + \overset{p}{1}A\overset{002}{\underset{\omega\mu\nu}{\alpha\beta r}} + \overset{p}{2}A\overset{112}{\underset{\omega\mu\nu}{\alpha\beta r}} + \overset{p}{3}A\overset{222}{\underset{\omega\mu\nu}{\alpha\beta r}} + \overset{p}{4}A\overset{110}{\underset{\omega\mu\nu}{\alpha\beta r}}\right.$$

$$+\overset{p}{5}A\overset{220}{\underset{\alpha\mu\nu}{\alpha\beta r}} + \overset{p}{6}A\overset{(12)3}{\underset{\omega\mu\nu}{\alpha\beta r}} + \overset{p}{7}A\overset{(12)1}{\underset{\omega\mu\nu}{\alpha\beta r}} + \overset{p}{8}A\overset{(20)2}{\underset{\omega\mu\nu}{\alpha\beta r}}$$

$$\left. +\overset{p}{9}A\overset{(10)3}{\underset{\omega\mu\nu}{\alpha\beta r}} + \overset{p}{10}A\overset{(20)0}{\underset{\alpha\mu\nu}{\alpha\beta r}} + \overset{p}{11}A\overset{(10)1}{\underset{\omega\mu\nu}{\alpha\beta r}}\right) B_{\alpha\beta r} = 0,$$

where

$$(7.2)a \quad \overset{p}{0} = k^2(16\,K^2 - 10\,K - 25\,k - 1), \quad .$$

$$(7.2)b \quad \overset{p}{1} = k\,(2\,K + 5\,k - 3),$$

$$(7.2)c \quad \overset{p}{2} = 2\,(1 + K - 2\,K^2 + k - K\,k),$$

$$(7.2)d \quad \overset{p}{3} = 2\,K + 5\,k - 3,$$

$$(7.2)e \quad \overset{p}{4} = 14\,k\,K - 4\,k\,K^2 + 4\,k + 4\,K^2 - 8\,K^3 - 1 + 2\,K + 5\,k^2,$$

$$(7.2)f \quad \overset{p}{5} = 2\,k\,K - 7\,k - 4\,K + 4\,K^2 + 1,$$

$(7.2)g$ $\quad \underset{6}{p} = 4\,(4K^2 - 2\,K - 5\,k - 1),$

$(7.2)h$ $\quad \underset{7}{p} = 4\,(8\,K^3 - 4\,K^2 - 2\,K - 12\,k\,K - 3\,k + 1),$

$(7.2)i$ $\quad \underset{8}{p} = 2\,(1 - 2\,K + k + 4\,k\,K),$

$(7.2)j$ $\quad \underset{9}{p} = 4\,(k\,K + 4\,k + K - 2\,K^2),$

$(7.2)k$ $\quad \underset{10}{p} = 2\,k\,(b\,K + 15\,k - 8\,K^2 - 1),$

(7.2) $\quad \underset{11}{p} = 2\,(10k\,K + 4k\,K^2 + 2\,k + 4\,K^2 - 8\,K^3 - 1 + 2\,K - 5k^2).$

In non-holonomic form equation (7.1) reduces to (3.3), (4.3), (5.3) and (6.3) respectively according as

$$1 - K - \sqrt{D} - 2\sqrt{k} = 0,$$
$$1 - K + \sqrt{D} - 2\sqrt{k} = 0,$$
$$1 - K - \sqrt{D} + 2\sqrt{k} = 0,$$
$$1 - K + \sqrt{D} + 2\sqrt{k} = 0.$$

PROOF. From equation (1.28)b, c, d it is obvious that when $a^2 - 4\,kb^2 = 0$, the expression

$$4\,\underset{1}{B}(K-1) + \underset{2}{B}(1 - 2\,K + 5\,k) + 2\,\underset{3}{B}(1 - 4\,K + 4\,K^2 - 5\,k)$$

is identically equal to zero.

Substituting the values of $\underset{1}{B}$, $\underset{2}{B}$ and $\underset{3}{B}$ in terms of $\underset{B}{pqr}$ from the equations (1.28) e, f, g we get the conditions (7.1).

To show that (7.1) includes all the four conditions of the non-holonomic form as given by (3.3), (4.3), (5.3) and (6.3), we can put (7.1) in the non-holonomic form and prove the desired results.

But in this case this process shall be very laborious. Hence instead of putting the conditions (7.1) in non-holonomic form, we put equations (1.27), from which these conditions are obtained, in non-holonomic form. Putting (1.27)a in non-holonomic form, and using (1.31), it reduces to

$$(7.3) \qquad S_{xyz} = \frac{1}{2\underset{xyz}{\lambda}} \left(K_{xyz} + 3\,\underset{x}{\lambda}\,\underset{y}{\lambda}\,K_{[xyz]} \right).$$

The other equations (1.27)b, by using (1.7) and (1.31) reduce to (7.3), multiplied on both sides by homogeneous functions of $\underset{x}{\lambda}$, $\underset{y}{\lambda}$, $\underset{z}{\lambda}$ of the form

$$\left(\underset{x}{\lambda^p}\,\underset{y}{\lambda^q} + \underset{x}{\lambda^q}\,\underset{y}{\lambda^p} \right) \underset{z}{\lambda^r} \qquad p, q \leqslant 2, r \leqslant 3.$$

This expression vanishes only in four cases when $x, y = 1$, 2 or 3,4 and $p,q = 1,0$ or 1,2. Consequently equations (1.27)b, c, e, f reduce to (7.3). Hence (7.3) is the non-holonomic form of the equation (1.27) (cf. Mishra [2] p. 882). Consequently the conditions for the existence of at least one solution of (1.27) in the non-holonomic form will be as given in (3.3), (4.3), (5.3) and (6.3).

THEOREM (7.2). *A necessary and sufficient condition for the existence of at least one solution $S_{\omega\mu\nu}$ of (1.19) in the first class when $D \neq 0$ and $a^2 - 4kb^2 = 0$ is (7.1).*

PROOF. Since the solution $S_{\omega\mu\nu}$ of (1.19) is to be obtained from the equations (1.27) when $a^2 - 4 kb^2 = 0$, the above Theorem follows from Theorem (7.1).

8. *Singular Solutions : $D \neq 0$, $a^2 - 4 kb^2 = 0$.*

We shall now give the solution in the halonomic form when $D \neq 0$ and $a^2 - 4 kb^2 = 0$.

THEOREM (8.1). *When the condition (7.1) is satisfied, the solution $S_{\omega\mu\nu}$ of (1.19) in the first class when $D \neq 0$ and $a^2 - 4 k b^2 = 0$ is*

$$(8.1) \qquad S_{\omega\mu\nu} = \tfrac{1}{3}\left(K_{\omega\mu\nu} + 3 \cdot k_{\omega}^{\alpha}\, k_{\mu}^{\beta}\, K_{[\alpha\beta\nu]} \right) + H_{\omega\mu\nu} ,$$

where $H_{\omega\mu\nu}$ is a tensor skew-symmetric in the first two indices.

Proof. The solution $S_{\omega\mu\nu}$ of (1.19) in the first class when $D \neq 0$ is given by (1.29) when $g (a^2 - 4kb^2) \neq 0$. When $a^2 - 4 kb^2 = 0$, (1.19) has at least one solution if (7.1) is satisfied. When $a^2 - 4 kb^2 = 0$, it is easily verified that the expression $4\, B_1 (K - 1) + B_2 (1 - 2 K + 5k) + 2\, B_3 (1 - 4 K + 4 K^2 - 5 k)$ is equal to zero. Hence the solution (1.29) reduces to the form (8.1).

Theorem (8.2). *When $D \neq 0$ and $1 - K - \sqrt{D} - 2 \sqrt{k} = 0$, the non-holonomic components H_{ijk} of the tensor $H_{\omega\mu\nu}$ occuring in the equation (20.1) are given by*

(8.2)a the components H_{faa} are arbitrary

when $a + f$ is odd,

(8.2)b the remaining H_{ijk} are given by

$$H_{ijk} = \left(1 - \frac{\lambda}{ijk} \right) S_{ijk} ,$$

where λ's are to be taken from (3.1) and 3.2) and S_{ijk} from equations (3.4)

Proof. When (7.1) is satisfied and $1 - K - \sqrt{D} - 2\sqrt{k} = 0$, the non-holonomic components S_{xyz} of $S_{\omega\mu\nu}$ in the first class are given by (3.4). Substituting these values of S_{ijk} in the non-holonomic form of (8.1) and using (1.31) and (3.1), we obtain (8.2).

Theorem (8·3). *When $D \neq 0$ and $1 - K + \sqrt{D} - 2\sqrt{k} = 0$, the non-holonomic components H_{ijk} of the tensor $H_{\omega\mu\nu}$ occuring in the equation (8.1) are given by*

(8.3)a   the components H_{aff} are arbitrary

when $a + f$ is odd,

(8.3)b   the remaining components H_{ijk} are given by

$$H_{ijk} = \left(1 - \frac{\lambda}{ijk}\right) S_{ijk},$$

where λ's are to be taken from (4.1) and (4.2) and S_{ijk} from equation (4.4).

Proof. The proof of this Theorem follows the pattern of the proof of Theorem (8·2).

Theorem (8·4). *When $D \neq 0$ and $1 - K - \sqrt{D} + 2\sqrt{k} = 0$, the non-holonomic components H_{ijk} of the tensor $H_{\omega\mu\nu}$ occuring in the equation (8.1) are given by*

(8·4)a   the components H_{faa} are arbitrary

when $a + f$ is even,

(8·4)b   the remaining H_{ijk} are given by

$$H_{ijk} = \left(1 - \frac{\lambda}{ijk}\right) S_{ijk},$$

where λ's are taken from (5.1) and (5.2) and S_{ijk} from equations (5.4).

Proof. The proof of this Theorem follows the pattern of the proof of Theorem (8.2).

Theorem (8.5). *When $D \neq 0$ and $1 - K + \sqrt{D} + 2\sqrt{k} = 0$ the non-holonomic components H_{ijk} of the tensor $H_{\omega\mu\nu}$ occuring in the equation (8.1) are given by*

(8·5)a   the components H_{aff} are arbitrary

when $a + f$ is even,

the remaining components H_{ijk} are given by

$$H_{ijk} = \left(1 - \frac{\lambda}{ijk}\right) S_{ijk} \, ,$$

where λ's are taken from (6.1) and (6.2) and S_{ijk} from equations (6.4).

Proof. The proof of this Theorem follows the pattern of the proof of Theorem (8.2).

9. *The tensor $U_{\omega\mu\nu}$* . We will now consider the tensor $U_{\omega\mu\nu}$. It has been shown in (Lal and Mishra [3] p. 234) that the solutions of (1.20)b in the first class are

$$(9.1)\left(U_{\omega\mu\nu} - C_{\omega(\mu\nu)}\right) g \,(a^2 - 4\, kb^2) = 4 \underset{1}{C}\,(K-1) \;+\; \underset{2}{C}\,(1 - 2K + 5k)$$
$$+\; 2 \underset{3}{C}\,(1 - 4\,K + 4\,K^2 - 5k)$$

where the symbol $\underset{r}{C}$ stands for $\underset{r}{C}_{\omega(\mu\nu)}$, and the values of $\underset{r}{C}$ are given by (1·28,e, f, g

when $\underset{r}{B}_{\omega\mu\nu}$ is replaced by $\underset{r}{C}_{\omega(\mu\nu)}$ and $\overset{pqr}{B}_{\omega\mu\nu}$ by $\overset{pqr}{C}_{\omega(\mu\nu)}$ and $C_{\omega\mu\nu} = K_{\omega\mu\alpha}\, k^{\alpha}_{\;\nu}$.

If the non-holonomic components of $h_{\lambda\mu}$, $h^{\lambda\mu}$, $(p)k_{\lambda}^{\;\nu}$ and $(p)k_{\lambda\mu}$ in the first class are given by (1.31), the solution $U_{\omega\mu\nu}$ of (1.20)b in the non-holonomic form is given by

$$(9.2)\qquad U_{xyz} = \frac{1}{2\underset{xyz}{\lambda}}\left(K_{xyz}{}^{\lambda}_{\;z} + K_{xyz}{}^{\lambda}_{\;y}\right)$$

with

$$(9.3)\qquad U_{(xyz)} = 0.$$

From the form of the solution (9.1) and (9.2) it is clear that the conditions for the degenerate cases for U are the same as they are for S.

Now the conditions for the existence of at least one solution $U_{\omega\mu\nu}$ of (1·20)b in the first class when $D \neq 0$ for the case $a^2 - 4\,kb^2 = 0$ will be found. The solution of (1.20)b will also be given for this case.

Theorem (9.1). *A necessary and sufficient condition for the existence of at least one solution $U_{\omega\mu\nu}$ of (1.20) in the first class when $D \neq 0$, $a^2 - 4\,kb^2 = 0$ is (7.1).*

Proof. The statement is obvious from Theorem (7.2) and equations (1.15)

Theorem (9.2). *When the condition (7.1) is satisfied the solution $U_{\omega\mu\nu}$ of (1.20)b in the first class when $D \neq 0$, $a^2 - 4kb^2 = 0$ is of the form*

$$(9\cdot4) \qquad U_{\omega\mu\nu} = \tfrac{1}{2}\left(K_{\omega\mu\alpha}\; k_\nu^\alpha + K_{\omega\mu\alpha}\; k_\mu^\alpha \right) + J_{\omega\mu\nu},$$

where $J_{\omega\mu\nu}$ is a tensor, symmetric in the last two indices

Proof. Substituting the conditions (7.1) in (9.1) and putting $a^2 - 4kb^2 = 0$, we find that the solution is of the form (9.4).

Theorem (9.3). *When the condition (7.1) is satified, the solution $U_{\omega\mu\nu}$ of (1.20)b in the first class when $D \neq 0$ and $I - K - \sqrt{D} - 2\sqrt{k} = 0$ has non-holonomic components (symmetric in the last two indices) in the form ($a \neq b$),*

(9.5)a   the components U_{aaf}, U_{faa} are arbitrary

        when $a + f$ is odd,

$$(9.5)b \quad U_{aaf} = \underset{aaf}{\frac{1}{2\lambda}} K_{afa}\;{}_a^\lambda, \quad a + f \text{ is even,}$$

$$(9.5)c \quad U_{faa} = \underset{faa}{\frac{1}{\lambda}} K_{faa}\;{}_a^\lambda, \quad a + f \text{ is even,}$$

$$(9.5)d \quad U_{efg} = \underset{efg}{\frac{1}{2\lambda}}\left(K_{efg}\;{}_g^\lambda + K_{egf}\;{}_g^\lambda \right),$$

$$(9.5)e \quad U_{efa} = \underset{efa}{\frac{1}{2\lambda}}\left(K_{efa}\;{}_a^\lambda + K_{eaf}\;{}_f^\lambda \right),$$

$$(9.5)f \quad U_{aef} = \underset{aef}{\frac{1}{2\lambda}}\left(K_{aef}\;{}_f^\lambda + K_{afe}\;{}_e^\lambda \right),$$

$$(9.5)g \quad U_{bed} = \underset{bed}{\frac{1}{2\lambda}}\left(K_{bed}\;{}_d^\lambda + K_{bdc}\;{}_c^\lambda \right),$$

$$(9.5)h \quad U_{abf} = \underset{abf}{\frac{1}{2\lambda}}\left(K_{abf}\;{}_f^\lambda + K_{afb}\;{}_b^\lambda \right),$$

$$(9.5)i \quad U_{fab} = \underset{fab}{\frac{1}{2\lambda}}\left(K_{fab}\;{}_b^\lambda + K_{fba}\;{}_a^\lambda \right),$$

where λ's are to be taken from (3.1) and (3.2).

[23]

Proof. Writing (1.15) in non-holonomic form and using (3.4), we obtain the non-holonomic components U_{ijk} of $U_{\omega\mu\nu}$.

Theorem (9.4). *When $D \neq 0$ and $1 - K - \sqrt{D} - 2\sqrt{k} = 0$ the non-holonomic components J_{ijk} of the tensor $J_{\omega\mu\nu}$ of ecuation (9 4), symmetric in the last two indices are given by*

(9.6)a   the components J_{aaf}, J_{faa} are arbitrary

when $a + f$ is odd.

(9.6)b   the remaining components J_{ijk} are given by

$$J_{ijk} = (1 - \overset{\lambda}{\underset{ijk}{}}) U_{ijk} \quad ,$$

where λ's are taken from (3.1) and (3.2) and U_{ijk} from (9.5).

Proof. Writing (9.4) in non-holonomic form and substituting the values of λ's from (3.1) and (3.2) and U_{ijk} from (9.5) respectively we get equations (9.6).

The solutions $U_{\omega\mu\nu}$ in the first class when $D \neq 0$, for the cases $1 - K + \sqrt{D} - 2\sqrt{k} = 0$, $1 - K - \sqrt{D} + 2\sqrt{k} = 0$ and $1 - K + \sqrt{D} + 2\sqrt{k} = 0$ can be derived similarly from (9.4).

The degenerate cases of the first class when $D = 0$ shall be considered in subsequent papers.

In conclusion I take this opportunity to thank Professor R. S. Mishra for his keen interest, advice and help in the preparation of this paper.

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ON THE PROCESSING OF ILFORD G-5 NUCLEAR EMULSIONS FOR DISTORTIONLESS TRACKS

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ABSTRACT

A procedure for processing Ilford G-5 emulsion plates for minimising the track distortion has been described. pH variations of the fixing solutions, swelling of the emulsions, shrinkage factors of the developed emulsions, etching or corrosion of emulsion grains and the clarity (transparency) of the emulsion plates have been studied for various fixing baths. It has been found that the addition of 2-2·5% ammonium sulphocyanide to the sodium bisulphite-fixing bath gives more preferable results.

1. INTRODUCTION

For a successful identification *i.e.* determination of mass, energy etc. of tracks caused by the passage of charged particles in nuclear emulsions, it will be a necessary condition that the characteristics of the tracks are not changed during the processing of the emulsions and hence to ensure the uniformity of development with depth and freedom from track curvatures due to the distortion of the emulsions.

In practice, great difficulties are encountered in processing the emulsions successfully (Kinoshita, 1910 and Michl, 1912). According to Dainton *et al* (1951), during ideal conditions the complete processing leads to a uniform contraction in the thickness of the emulsion which shrinks to about half its original thickness due to the removal of a large quantity of silver halide during the process of fixing. Due to the relative shifts of different layers of an emulsion caused by their expansion and contraction (swelling and shrinking) in different stages of processing, the stresses are introduced and cause track distortion. The abrupt and undue volume changes in emulsion may be due to several factors *e.g.* mechanical agitation, temperature variations, pH changes and removal of the large quantity of unaffected (unreduced) silver halide from the emulsion. The distortions affect the measurement of range, grain density, gap length densities, angles between tracks, δ-ray counting and the multiple coulomb scattering of the particle tracks. Hence, it emphasizes the importance of processing thick emulsions with a minimum of distortion.

Hopper *et al* (1954), Marguin (1957), Yagoda (1957) have tried isothermal processing of thick emulsions at low temperatures to reduce the swelling and hence the distortion in emulsions. Dilworth *et al* (1951) have given precautions required in fixing, washing and drying stages of the emulsions in order to minimize the distortion.

Many authors *e. g.* Lumiere *et al* (1908, 1948), Piper (1913, 1914, 1948), Karge (1925, 1948), Wilson and Vaneslow (1949), Dainton *et al* (1951), and Stiller *et al* (1954) have made use of Ammonium chloride in fixing bath to reduce the time of

fixing which was considered vitally responsible for producing distortion and have reported that its addition affects the surface layer grains of the emulsion. In one of the publications from this laboratory (Prakash *et al*, 1958), it has been shown that the etching or corrosion effect of grains on the surface of the emulsions is found to be negligible by using a particular concentration of ammonium chloride added to the fixing bath. Experimental studies of reducing 'corrosion' or ·dissolution of silver grains from thick nuclear emulsions ·in the fixing bath have been made by Meulemans (1954), Thuro and Paic (1956), Paic *et al* (1957) and Heughebaert and Heughebaert (1959) in must of the cases by eliminating oxygen from the fixer and adding either sodium bisulphite or sodium sulphite and acetic acid.

As most of the changes are affected during the fixing stage of the emulsions, it was thought useful to study the processing of electron-sensitive Ilford G-5 emulsions with special details of the fixing solutions.

2. EXPERIMENTS

An experimental study was made on the most standard G-5 emulsion plates of different thicknesses viz. 100 μ, 200 μ, 400 μ, and 600 μ. The plates were processed in a thermostatically controlled cooling Cabinet (T. C. C. Cabinet) and were kept horizontal throughout the processing with glass surface downwards. The procedure of processing followed by us is given below :—

(1) Development process.

(a) *Presoaking.* Each emulsion plate was immersed in distilled water at room temperature before being put in the developer and then the water was cooled down to 5°c and maintained at this temperature for a period shown in Table 2.

(b) *Temperature-cycle development.* For development of the emulsions temperature —cycle method was employed (Dilworth *et al*, 1950; Bonetti *et al*, 1951). In the cold stage of the developer penetration a constant temp. of 5°C was maintained to allow a minimum development. For the main development process warm 'dry' development i.e. hot plate development was done at a temp. of 18°C and proper care was taken to ensure a good thermal contact between the glass surface of the emulsion plates and the dry surface of a stainless steel box put in one compartment of the T. C. C. Cabinet and surrounded by a water bath maintained at the required temperature. The times for development are shown in Table 2.

The development was done in amidol developer. For 100 μ and 200 μ thick plates, normal amidol develper (pH = 7·2) was used while for 400 μ and 600 μ thick plates Brussels amidol developer (pH = 6·6) was employed. The formulae for these two developers are given in Table 1.

TABLE 1

Developers used

Name of developer	Normal amidol developer	Brussels amidol developer
pH value	7·2	6·6
Formula used ...	Amidol 3·0 gm. Sodium Sulphite (anh.) 12·0 gm. Distilled water 1 litre	Amidol 4·5 gm. Sodium Sulphite (anh.) 18·0 gm. Boric acid 35·0 gm. Pot. Bromide (10 % Sol.) 8 c.c. Distilled water 1 litre.

The amidol developer was used because it creates uniformity and low background in comparison to that with other developers (Dainton *et al*, 1951; Herz, 1952).

(*c*) *Stop bath.* After development, the emulsion plates were transferred to a stop bath (0·75% solution of acetic acid in water) at the same temp. as that of the hot plate and the temp. of the stop bath was then gradually reduced down to 5°C. The plates were kept in this bath for the time shown in Table 2.

(*d*) *Removal of surface deposit.* The thin film of silver which is usually formed on the surface of the emulsion during development process due to the high concentration of silver bromide in nuclear emulsions, was gently and carefully wipped off in the stop bath by means of a wet soft cotton.

2. Fixation.

After complete treatment upto the stop bath, each set of the plates was transferred to the following fixing baths :—

(*i*) Pure hypo bath made from 35% solution of sodium thiosulphate in water. The pH value of this bath (when freshly prepared) was 7·6.

(*ii*) The fixing bath of pH equal to 5·0 made from the following formula :—

Sodium thiosulphate	...	350 gm.
Sodium bisulphite (anh.)	...	30 gm.
Water	...	1 litre.

(*iii*) The above sodium bisulphite-fixing bath with the addition of the optimum concentrations of the following ammonium salts :—

(*a*) 1-1·5% solution of amm. chloride (*i. e.* 1-1·5 gm. of amm. chloride salt added to 100 c.c. of the fixing bath).

(*b*) 2% solution of amm. hydroxide.

(*c*) 2-2·5% solution of amm. sulphocyanide.

The use of above mentioned concentrations of ammonium salts was made because of their best results in minimising the fixing time (Prakash *et al*, 1958). The use of sodium sulphite in the above fixing baths was prefered due to the fact that it reduces stains in the finally processed emulsion (Mees, 1948 ; Dainton *et al* 1951). Thuro and Paic (1956) have recommended the use of either sodium bisulphite or sodium sulphite plus acetic acid with hypo baths as it inhibits the dissolution of silver grains in emulsions.

The emulsion plates were kept in a static fixing bath *i.e.* no agitation was done during fixing, but simultaneously the bath was changed very frequently. The first change of the fixing bath was done after a period equal to one-third the required time of clearing the plates (without taking into account the dilution time). The rest of the changes of baths were made at regular intervals. After the first stage of fixing (*i.e.* clearing) at constant concentration, the fixing baths were diluted regularly. Throughout the fixing process, a constant temp. of 5°C was maintained and the total time given for fixing the emulsion plates was nearly equal to one and half times the clearing time or more. The fixing times for different emulsions are shown in Table 2.

(3) Washing.

The washing of the emulsion plates was done in cold water in one of the compartments of a T. C. C. cabinet. The tap water was allowed to trickle in very slowly at the time of the last stage of fixing in the large dishes containing emulsion plates and simultaneously the water was allowed to go out of the dishes by means of a siphon arrangement. During this process, the cooling cabinet was worked out continuously for cooling the water of the dishes. Slowly and slowly, the rate of flow of water and its temperature was increased. The washing process was considered complete when the washing bath of the dish stopped giving an indication of the presence of hypo observed by the hypo indicator solution of potassium permanganate.

(4) Drying.

Before drying, the plates were put in a dish containing 1·5% solution of glycerine to prevent the stripping off in the emulsions from the glass surface. After taking out from the glycerine solution the emulsion plates were arranged on a stainless steel box previously placed in a cooling cabinet and were left for drying. The temperature of the cabinet was raised slowly.

The above complete procedure for processing the thick Ilford G-5 emulsion plates is outlined in Table 2.

TABLE 2

Processing time and temperature conditions for Ilford G-5
emulsions of different thicknesses

Procedure		Temp.	Time for			
			100 μ	200 μ	400 μ	600 μ
Presoaking	...	Room Temp. →5°C.	20 min.	30 min.	100 min.	150 min.
Development						
(a) Cold Stage	...	5°C.	20 min.	30 min.	100 min.	150 min.
(b) Hot Stage	...	18°C.	30 min.	40 min.	120 min.	180 min.
Stop bath	...	18°C.→5°C.	20 min.	25 min.	100 min.	150 min.
Fixation						
(a) Clearing	...	5°C.	3 hrs.	6 hrs.	40 hrs.	80 hrs.
(b) Dilution	...	5°C.	2 hrs.	4 hrs.	24 hrs.	30 hrs.
Washing	...	5°C. — 10°C.	3 hrs.	6 hrs.	30 hrs.	50 hrs.
Glycerine bath	...	5°C.	10 min.	10 min.	30 min.	1 hr.
Drying	...	5°C.→ Room Temp.	12 hrs.	18 hrs.	4 days	6 days

During the fixing process, the pH values of the fixing baths and the swelling of the emulsions for 600 μ thick plates were measured at regular intervals and the results obtained are shown in figs. 1 and 2.

Fig. 1. Variation of pH of solutions with time during the fixing process : (1) pure hypo bath, (2) Fixing bath by adding Sodium bisulphite to the pure hypo bath, (3) Amm. chloride added to fixing bath, (4) Amm. hydroxide added to fixing bath and (5) Amm. Sulphocyanide added to fixing bath.
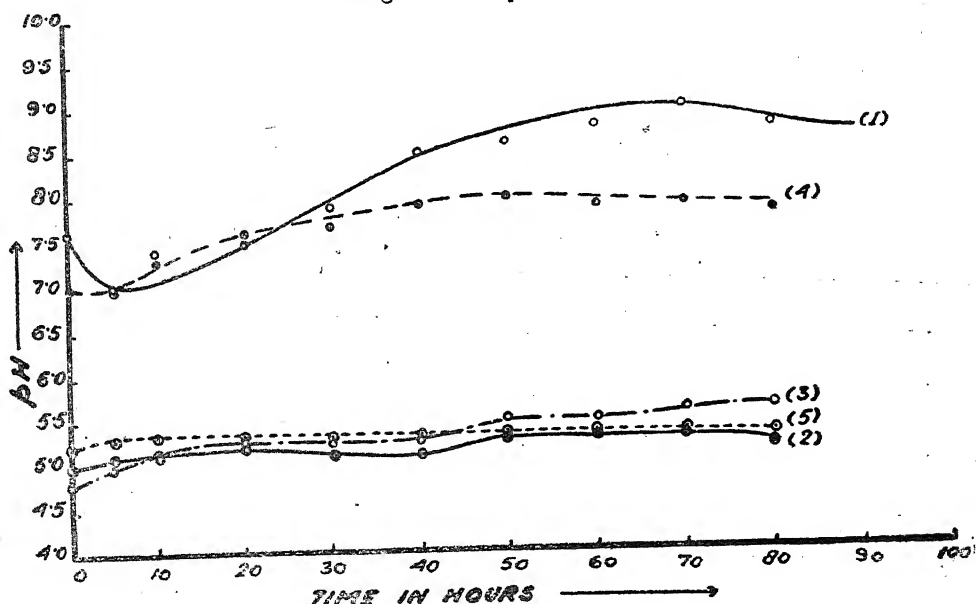

Fig. 2. Variation of swelling of emulsions with time during the fixing process : (1) pure hypo bath. (2) Fixing bath by adding sodium bisulphite to the pure hypo bath, (3) Amm. chloride added to fixing bath, (4) Amm. hydroxide added to fixing bath and (5) Amm. Sulphocyanide added to fixing bath.
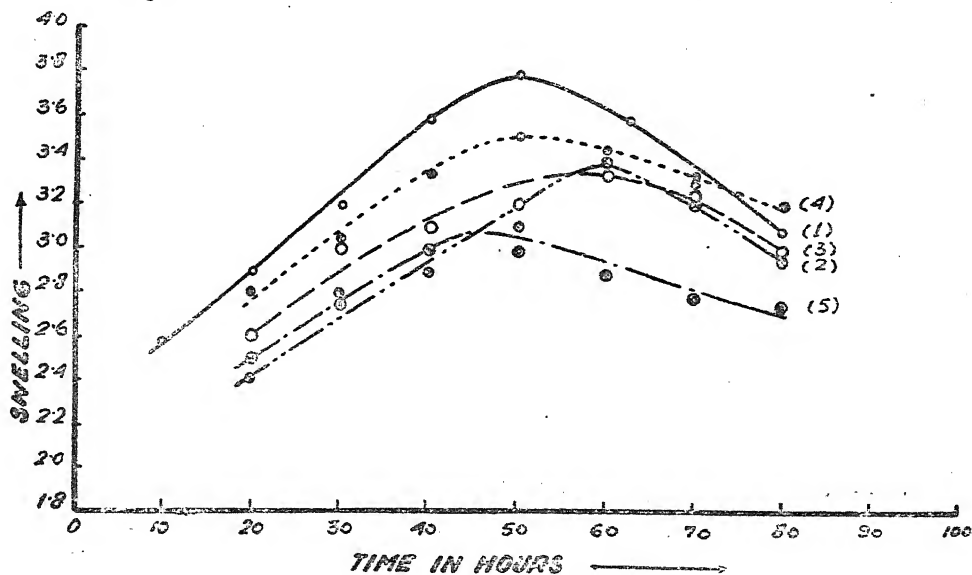
[29]

The clearing time of the thick emulsion plates in different ammonium-fixing baths and the swelling ratio (*i.e.* the ratio of the thickness of emulsion at maximum swelling to that before processing) for thick emulsions (600 μ) are also shown in Table 3.

TABLE 3

Clearing time and swelling in ammonium-fixing baths

Ammonium-fixing bath	Clearing time for					Swelling ratio for 600μ emulsions
	100μ	200μ	400μ	600μ	1000μ	
Amm. chloride bath	74 min.	248 min.	15·5 hr.	29·0 hr.	68 hr.	3·82
Amm. hydroxide bath	88 min.	260 min.	16·5 hr.	36·5 hr.	84 hr.	4·00
Amm. Sulphocyanide bath	44 min.	222 min.	15·0 hr.	33·0 hr.	...	3·41

Fig. 3 shows the variation of grain density with depth in some of the minimum ionization (relativistic) tracks of cosmic radiation in 600μ thick emulsions processed according to the above mentioned procedure and fixed in the ammonium sulphocyanide-fixing bath. The average diameter of grains in different emulsion plates with the depth of the emulsion was also observed and found nearly the same within statistical errors (Prakash *et al* 1958).
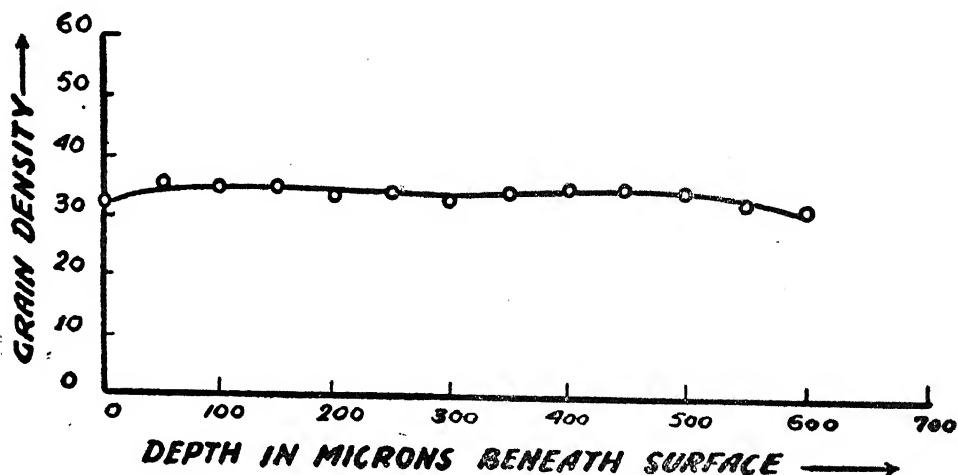
Fig. 3. Variation of grain density per 100 micron with depth of the emulsion beneath the top (air) surface for minimum ionization (relativistic) tracks of cosmic radiation found in G-5 (600 μ) plates fixed in Amm. sulphocyanide-fixing bath after the development process.

It was significant to note that no curvature of tracks (C-shaped or S-shaped distortion) due to the differential shear along the deeply dipping tracks of energetic particles could be observed and no appreciable departure from rectilinearity could be recorded for such tracks under the microscope. Even for low energy tracks the

deviations, if any, from the straight path of the track were due to the multiple Coulomb scattering of the particle and not due to the distortion of the tracks. The validity of the above inference depended on three independent methods of measurement *i.e.* grain density, mean gaplength and the multiple scattering. For scattering measurements the constant sagitta method according to the scheme of Fay *et al* (1954) was used.

The table 4 gives the experimental values of shrinkage factors of the emulsion plates which are obtained from the ratio of the emulsion thickness before processing to that after the complete processing and which can directly be measured, as the difference in depth between the highest and the lowest fog grains visible by means of the calibrated fine depth adjustment of the microscope.

TABLE 4

The shrinkage factors of the plates developed simultaneously but fixed in different baths

Thickness of the plates in microns	Shrinkage factors				
	Free hypo	Fixing bath	Fixing bath having optimum conc. of		
			Amm. chloride	Amm. Hydroxide	Amm. Sulphocyanide
100 ...	2·00	2·30	2·30	2·18	2·19
200 ...	2·60	2·52	2·65	2·53	2·52
400 ...	2·45	2·46	2·52	2·40	2·41
600 ...	2·55	2·53	2·55	2·51	2·54

3. DISCUSSION OF RESULTS AND CONCLUSION

It is clear from table 3 that the addition of sulphocyanide to fixing bath reduces the clearing time by maximum amount in comparison to the other salts. The swelling ratio is also minimum in the case of Sulphocyanide-fixing bath. This is due to the fact that Amm. Thio sulphate is a better complex making reagent as compared to sodium thiosulphate itself and increases the rate of diffusion of fixation.

Fig 1. Shows that the Sod. bisulphite-fixing bath with optimum concentration of amm. sulphocyanide shows a constancy or stability of pH value throughout the clearing process. This ensures the reduction in distortion which are caused by the changes in the pH concentration of the fixing baths during the processing of the emulsions. The pure hypo bath and the amm. hydroxide-fixing bath show an unstable high value of pH which reduces the diffusion velocity and makes the baths much alkaline, while the other baths indicate an acidity. The brownish colour

of plates in amm. hydroxide-fixing bath may be due to the alkaline property of the solution.

Fig. 2 clearly indicates that the maximum variation in the swelling is found in the case of pure hypo bath while the minimum variation in swelling is seen in the case of amm. sulphocyanide fixing bath. The other curves show the intermediate values of swelling. This again ensures a considerable reduction in the abrupt volume or stress changes (*i.e.* swelling and shrinking) and hence may minimise the track distortions. The curves of Figs. 1 and 2 both indicate that the addition of amm. hydroxide to fixing baths is never desirable.

The results of table 4 show that the values of the shrinkage factors for different plates are similar within statistical errors. These results and also the results of Fig. 3 indicate that the gelatin or grains have not been affected by the ammonium fixing baths. If it would have been so, the shrinkage factors should have been higher in these cases. Powell, Fowler and Perkins (1959) have also stated that even in well developed emulsion plates the fall in grain density along the relativistic track near the surface of the emulsion is due to 'etching' caused by a chemical attack on the silver of the developed grains as a result of prolonged fixation or some action in the clearing bath. It is clear that the addition of ammonium salts (at optimum concentration) to fixing baths have no chemical effect of etching (corrosion) or dissolution of grains of the emulsions.

The thick emulsion plates processed according to the procedure described in the present paper and fixed in a fixing bath by adding to it an optimum concentration (2-2·5%) of the ammonium sulphocyanides olution are found very satisfactory.

Thus from all considerations *e. g.* the uniform development of emulsions ; freedom from track distortion, background grains, etching or corrosion of surface grains ; clarity of plates ; pH value of fixing bath ; shrinkage factor and the maximum reduction in clearing time, the use of ammonium sulphocyanide salt with 35% hypo bath is preferred.

4. ACKNOWLEDGMENT

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ON n-OPERATIONAL RELATIONS IN A CHAIN

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1. Let

$$\phi(p) = p \int_0^\infty e^{-pt} f(t)\, dt, \ \mathrm{R}(p) > 0,$$

then we shall say that $\phi(p)$ is operationally related to $f(t)$ and this relation is symbolically denoted by

$$\phi(p) \doteqdot f(t) \text{ or } f(t) \doteqdot \phi(p)$$

In a recent paper (2) we have established the result ;

If $\quad \phi(p) \doteqdot x^{\gamma-2} \Psi(x),$

$$\Psi(p) \doteqdot f(x),$$

$$f(p) \doteqdot h(x),$$

$$p^{-2\nu} h\left(\frac{1}{p}\right) \doteqdot g(x) \text{ and}$$

$$\mathrm{F}(p) \doteqdot x^{\frac{1}{2}-\nu-l} g(x), \text{ then}$$

$$(1.1) \qquad p^{\gamma-1} \phi(p) = \int_0^\infty t^{l-\nu-\frac{5}{2}}\, \mathrm{E}\left(2, 2+\nu, \gamma : \nu-l+\tfrac{5}{2} : pt\right)\mathrm{F}\left(\frac{1}{t}\right) dt$$

provided the conditions in

$$(1.2) \left(\mathrm{R}(p) > 0, \ \mathrm{R}(2+2\nu) > 0, \ \mathrm{R}(\mu) > -1, \ \mathrm{R}(\mu+2\nu) > -1 ; \ \mathrm{F}\left(\frac{1}{t}\right) t^{l-\nu-\frac{1}{2}}\right.$$

is $0\ (t^\rho)$ for large t, where $\mathrm{R}(2-\rho) > 1$ and is $0(t^\mu)$ for small t; $\mathrm{R}(\gamma) > 0, \mathrm{R}(\mu+\gamma-1)$

$> 0 \Big)$ are satisfied.

The object of this paper in the first instance is to extend the result in (1.1) by introducing one more operational relation in the chain, given above, of the transforms and ultimately to develop this into a chain, connecting n-operational relations.

2. We now state theorem :

Theorem 1.

$$\text{If } \chi_1(p) \doteqdot x^{\gamma_1} \ \phi\left(\frac{1}{x}\right),$$

$$\phi(p) \doteqdot x^{\gamma - 2} \ \Psi(x),$$

$$\Psi(p) \doteqdot f(x),$$

$$f(p) \doteqdot h(x),$$

$$p^{-2\nu} h\left(\frac{1}{p}\right) \doteqdot g(x),$$

$$F(p) \doteqdot x^{\frac{1}{2} - \nu - l} g(x), \text{ then}$$

(2.1) $\quad p^{\gamma + \gamma_1 - 1} \chi_1(p) = \int_0^\infty x^{l - \nu - \frac{5}{2}} E\left(2, 2 + 2\nu, \gamma, \gamma + \gamma_1 : \nu - l - \frac{5}{2} : px\right) \times$

$$\times F\left(\frac{1}{x}\right) dx$$

provided the conditions stated in (1.2) are satisfied and

$$R(\gamma + \gamma_1) > 0, \ R(\mu + \gamma + \gamma_1 - 1) > 0.$$

Proof :—

$$\chi_1(p) = p \int_0^\infty e^{-pt} t^{\gamma_1} \phi\left(\frac{1}{t}\right) dt$$

Substituting for $\phi(t)$ from (1.1), we get

(2.2) $\quad \chi_1(p) = p \int_0^\infty e^{-pt} t^{\gamma + \gamma_1 - 1} dt \int_0^\infty x^{l - \nu - \frac{5}{2}} E\left(2, 2 + 2\nu, \gamma : \right.$

$$\left. \nu - l + \frac{5}{2} : \frac{x}{t}\right) F\left(\frac{1}{x}\right) dx$$

On inverting the order of integration, we get

(2.3) $\chi_1(p)$

$$= p \int_0^\infty x^{l - \nu - \frac{5}{2}} F\left(\frac{1}{x}\right) dx \int_0^\infty e^{-pt} t^{\gamma + \gamma_1 - 1} E\left(2, 2 + 2\nu, \gamma : \nu - l + \frac{5}{2} \frac{x}{t}\right) dt$$

$\mid$ 35 $\mid$

Making use of the results (MacRobert, 1941, (1)}

$$(2.4) \quad \int_0^\infty e^{-\lambda} \lambda^{\beta-1} E\left(p \; ; \; \alpha_r : q, \; \rho_s : \frac{x}{\lambda}\right) d\lambda = E\left(p+1 : \alpha_r : q ; \rho_s : x\right)$$

where $\alpha_{p+1} = \beta$ and $R(\beta) > 0$, $R(x) > 0$, wet get

$$(2.5) \quad p^{\gamma+\gamma_1-1} \chi_1(p) = \int_0^\infty x^{l-\nu-\frac{5}{2}} E\left(2, 2+2\nu, \gamma, \gamma+\gamma_1 : \nu-l+\frac{5}{2} : px\right) F\left(\frac{1}{x}\right) dx$$

$(R(\gamma) > 0, \; R(\gamma+\gamma_1) > 0, \; R(2+2\nu) > -1, \; R(\mu+\gamma-1) > 0, \; R(\mu+\gamma+\gamma_1-1) > 0, \; R(p) > 0)$

The inversion in the order of integrations is justifiable since ;

(i) the x-integral in (2.2) is absolutely convergent under conditions of (1.2)

(ii) the t-integral in (2.3) is absolutely convergent for $R(p) > 0$, $R(\gamma+\gamma_1) > 0$ and

(iii) By our assumptions vide (1.2) $t^{l-\nu-\frac{1}{2}} F\left(\frac{1}{t}\right)$ is $O\left(t^\rho\right)$ for large t where $R(2-\rho) > 1$ and is $o\left(t^\mu\right)$ for small t where $\mu > -1$, $\mu+2\nu > -1$.

It is easy to see, that under these conditions (conditions of 1.2) the integral in (2.5) is absolutely convergent provided further that $R(\mu+\gamma+\gamma_1-1) > 0$. This proves the theoren.

Next let us suppose that the Laplace transform of $\chi_1\left(\frac{1}{x}\right) x^{\gamma_2}$ is $\chi_2(x)$, so that

$$\chi_2(p) = p \int_0^\infty e^{-pt} \chi_1\left(\frac{1}{t}\right) t^{\gamma_2} dt,$$

the integral on the right being assumed to be absolutely convergent.

On substituting for $\chi_1(p)$ from (2·5) and inverting the order of integrations, we get

$$p^{\gamma+\gamma_1+\gamma_2-1} \chi_2(p) = \int_0^\infty x^{l-\nu-\frac{5}{2}} F\left(\frac{1}{x}\right) dx \int_0^\infty e^{-t} t^{\gamma+\gamma_1+\gamma_2-1} E\Big(2, 2+2\nu,$$

$$\gamma+\gamma_1 : \nu-l+\frac{5}{2} : \frac{px}{t}\Big) dt$$

Evaluating the t-integral with the help of (2.4), we get

$$(2.6) \quad p^{\gamma+\gamma_1+\gamma_2-1} \chi_2(p)$$

$$= \int_0^\infty x^{l-\nu-\frac{5}{2}} E\Big(2, 2+2\nu, \gamma, \gamma+\gamma_1, \gamma+\gamma_1+\gamma_2 : \nu-l+\frac{5}{2} : px\Big) F\left(\frac{1}{x}\right) dx$$

where conditions of theorem 1 are satisfied with the additional conditions that $R(\gamma + \gamma_1 + \gamma_2) > 0$ and $(R(\mu + \gamma + \gamma_1 + \gamma_2 - 1) > 0$. Now (2.6) is exactly similar in form to (2.5) except for the additional parameter γ_2 on the left and $\gamma + \gamma_1 + \gamma_2$ in the E-function on the right. This suggests that this process can be repeated any number of times, each repetition having the effect of introducing additional terms as aforesaid. Thus following the above line of proof repeatedly, we shall generalise theorem 2 in the following form. Thus,

Theorem 3 :

$$\text{Let } \chi_n(p) \doteqdot x^{\gamma_n} \chi_{n-1}\left(\frac{1}{x}\right)$$

$$\chi_{n-1}(p) \doteqdot x^{\gamma_{n-1}} \chi_{n-2}\left(\frac{1}{x}\right)$$

$$\vdots \qquad \vdots$$

$$\vdots \qquad \vdots$$

$$\chi_2(p) \doteqdot x^{\gamma_2} \chi_1\left(\frac{1}{x}\right)$$

$$\chi_1(p) \doteqdot x^{\gamma_1} \phi\left(\frac{1}{x}\right)$$

$$\phi(p) \doteqdot x^{\gamma-9} \psi(x)$$

$$\psi(p) \doteqdot f(x)$$

$$f(p) \doteqdot h(x)$$

$$p^{-2\nu} h\left(\frac{1}{p}\right) \doteqdot g(x). \text{ and}$$

$$F(p) \doteqdot x^{\frac{1}{2} - \nu - l} g(x), \text{ then}$$

$$\gamma + \gamma_1 + \gamma_2 + \ldots\ldots + \gamma_n - 1 \, \chi_n(p)$$

$$= \int_0^\infty x^{l-\nu-\frac{5}{2}} E\left(2, 2 + 2\nu, \gamma, \gamma + \gamma_1, \gamma + \gamma_1 + \gamma_2, \ldots\ldots, \gamma + \gamma_1 + \gamma_2 \right.$$
$$\left. + \ldots + \gamma_n: \nu - l + \tfrac{6}{2}: px\right) F\left(\frac{1}{x}\right) dx,$$

where conditions of Theorem 1 are satisfied and $R(\gamma + \gamma_1 + \ldots + \gamma_n) > 0$ for $n = 2, 3, \ldots, n$: and $R(\mu + \gamma + \gamma_1 + \ldots\ldots + \gamma_n - 1) > 0$ for $n = 2, 3, \ldots, n$.

In conclusion I wish to express my sincerest thanks to Dr. S. C. Mitra for help in the preparation of this paper.

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[37]

STUDIES ON THE VELOCITY OF FLOW OF LIQUIDS THROUGH ADSORBENT COLUMNS

PART XI. RELATION BETWEEN THE RATE OF FLOW (v/t) AND INVERSE OF THE HEIGHT (1/h) OF THE COLUMN

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ABSTRACT

The velocities of flow or the liquid transmission capacities (v/t) of water, methyl alcohol, methyl acetate, acetone and benzene through adsorbent columns of calcium carbonate, silicic acid, Fuller's earth, Kieselguhr and magnesium oxide, have been determined and plotted against the inverse of the heighs ($1/h$) of the columns. The curves which are almost linear show that the velocity of flow is inversely proportional to the height with nearest approximation. The orders of liquid transmission give a method for the gradation of different adsorbents and indicate interesting evidences to show the importance of surface properties and the liquid structure.

In the previous communications[1-3], the authors have derived an empirical equation $\frac{vh}{t} \cdot \frac{\eta}{d} = K$, for the flow of organic liquids through different adsorbent columns, where v is the volume of a liquid flown through h, the height of the adsorbent column in time t ; η and d are the viscosity and density of the liquid. While deriving the above equation, it was assumed[3] that (i) v/t is proportional to $1/h$ and (ii) vh/t is proportional to d/η. It has been experimentally proved in an earlier communication[4] that vh/t is directly proportional to d/η. In the present communication, the authors have interpreted graphically the relationship between the rate of flow of liquids and the inverse of the height of the adsorbent columns. The orders of liquid transmissions of water, methyl alcohol, methyl acetate, acetone and benzene through calcium carbonate, silicic acid, Fuller's earth, Kieselguhr and magnesium oxide have been given in order to form an idea about the gradation of different adsorbents and with a view to showing the importance of surface properties and liquid structure.

EXPERIMENTAL

The details of the experimental technique for filling the adsorbents in the chromatographic tube and for measuring the rate of flow of liquids through columns packed with the same graded size of particles of the adsorbents under a constant suction pressure have been described earlier[1]. The rate of flow of a liquid was measured at a particular height of an adsorbent column. The height of the column was successively increased, and rates of flow were measured at different heights of adsorbent columns under similar conditions. The data for v/t and $1/h$ have been recorded in table nos. 1—5 and their graphical analysis is represented by curve nos. 1, 2, 3, 4 and 5.

TABLE 1

Height of mercury in the manometer = 34·5 cms. Temp. = 21·5 ± 1°C

Liquid	Calcium carbonate		Silicic acid		Magnesium oxide		Kieselguhr		Fuller's earth	
	1/h (cms.)	v/t	1/h	v/t	1/h	v/t	1/h	v/t	1/h	v/t
Water	·6680	·0117	·8688	·0236	·7092	·0378	·5856	·0339	·6869	·0036
	·4960	·0086	·4180	·0155	·3349	·0187	·4709	·0282	·4055	·0025
	·3125	·0061	·2847	·0112	·2836	·0167	·2841	·0180	·3191	·0020
	·2349	·0049	·2278	·0092	·2087	·0126	·2381	·0156	·2334	·0018
	·1852	·0041	·1709	·0070	·1949	·0118	·1831	·0121	·1731	·0013
	·1618	0036	·1552	·0063	·1600	·0097	·1604	·0106	·1471	·0011
	·1379	·0031	·1323	·0054	·1341	·0081	·1361	·0090	...	...

TABLE 2

Liquid	Calcium carbonate		Silicic acid		Magnesium oxide		Kieselguhr		Fuller's earth	
	1/h (cms.)	v/t	1/h	v/t	1/h	v/t	1/h	v/t	1/h	v/t
Methyl alcohol	·5879	·0109	·6848	·0208	·8696	·0201	·6963	·0208	·7964	·0134
	·3451	·0068	·3827	·0121	·4132	·0177	·4202	·0149	·4525	·0083
	·2533	·0050	·2876	·0093	·2878	·0129	·2996	·0112	·3304	·0064
	·2169	·0044	·2222	·0072	·2485	·0112	·2385	·0093	·2222	·0048
	·1907	·0040	·1879	·0062	·1831	·0083	·2222	·0087	·1871	·0042
	·1509	·0031	·1506	·0051	·1465	·0064	·1727	·0069	·1603	·0036
	·1341	·0028	·1380	0047	...	...	·1563	·0062	·1316	·0030

TABLE 3

Liquid	Calcium carbonate		Silicic acid		Mangesium oxide		Kieselguhr		Fuller's earth	
	$1/h$	v/t	$1/h$	v/t	$1/h$	v/t	$1/h$	v/t	$1/h$	v/t
Methyl acetate	·7011	·0254	·5781	·0557	·5129	·1263	·6516	·0893	·6448	·0625
	·4272	·0185	·3408	·0340	·3294	·0891	·3460	·0484	·4504	·0486
	·3116	·0151	·2398	·0245	·2245	·0666	·2549	·0360	·2947	·0320
	·2438	·0125	·2222	·0233	·1744	·0535	·2222	·0333	·2222	·0245
	·1843	·0096	·1787	·0188	·1464	·0457	·1938	·0299	·1925	·0214
	·1590	·0083	·1558	·0164	·1345	·0424	·1497	·0288	·1579	·0176
	·1342	·0070	...	...	...	...	·1381	·0221	·1379	·0153

TABLE 4

Liquid	Calcium carbonate		Silicic acid		Magnesium oxide		Kieselguhr		Fuller's earth	
	$1/h$	v/t	$1/h$	v/t	$1/h$	v/t	$1/h$	v/t	$1/h$	v/t
Acetone	·6151	·0553	·8000	·0766	·6580	·1079	·6065	·0587	·6103	·0404
	·3363	·0308	·3906	·0383	·3334	·0617	·5000	·0564	·3475	·0240
	·2748	·0263	·2898	·0290	·2198	·0447	·2954	·0374	·2701	·0191
	·2350	·0237	·2222	·0233	·1724	·0373	·2222	·0294	·2222	·0159
	·1938	·0195	·1797	·0188	·1534	·0343	·1923	·0282	·1925	·0138
	·1599	·0161	·1592	·0167	·1307	·0293	·1541	·0233	·1640	·0116
	·1399	·0141	...	...	...	...	·1341	·0205	·1380	·0099

TABLE 5

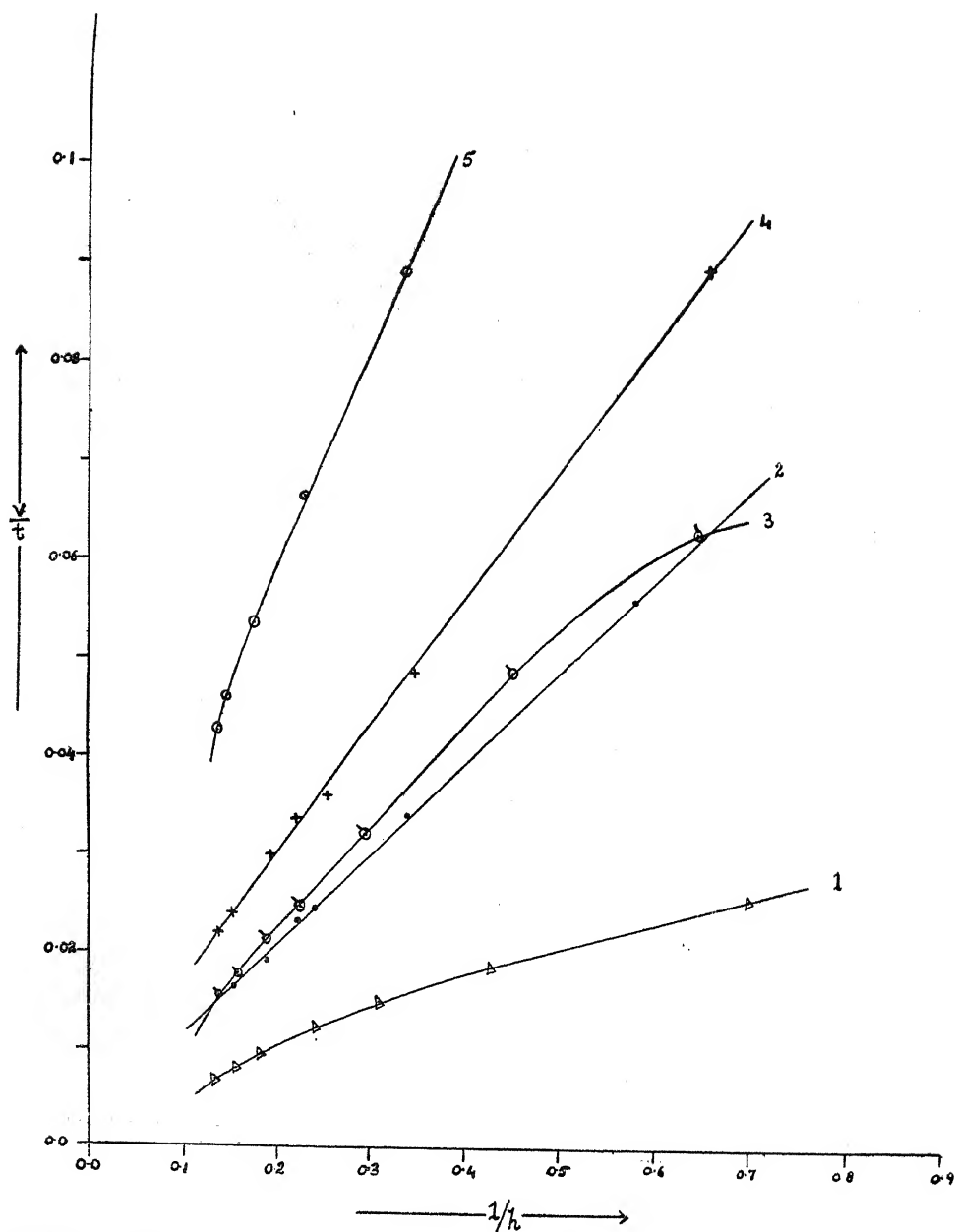| Liquid	Calcium carbonate		Silicic acid		Magnesium oxide		Kieselguhr		Fuller's earth	
	$1/h$	v/t	$1/h$	v/t	$1/h$	v/t	$1/h$	v/t	$1/h$	v/t
Benzene	·8104	·1177	·6756	·0562	·6153	·0581	·5483	·0866	·6789	·0455
	·4303	·0718	·4444	·0410	·2941	·0296	·4941	·0801	·3904	·0309
	·2808	·0505	·2563	·0290	·2211	·0250	·3311	·0576	·2560	·0211
	·2140	·0396	·2222	·0256	·1745	·0219	·2367	·0429	·2222	·0187
	·1861	·0349	·1862	·0218	·1443	·0200	·2222	·0405	·1774	·0165
	·1590	·0298	·1588	·0183	·1377	·0193	·1851	·0339	·1558	·0156
	·1347	·0252	...	...	...	...	·1538	·0283	·1341	·0135
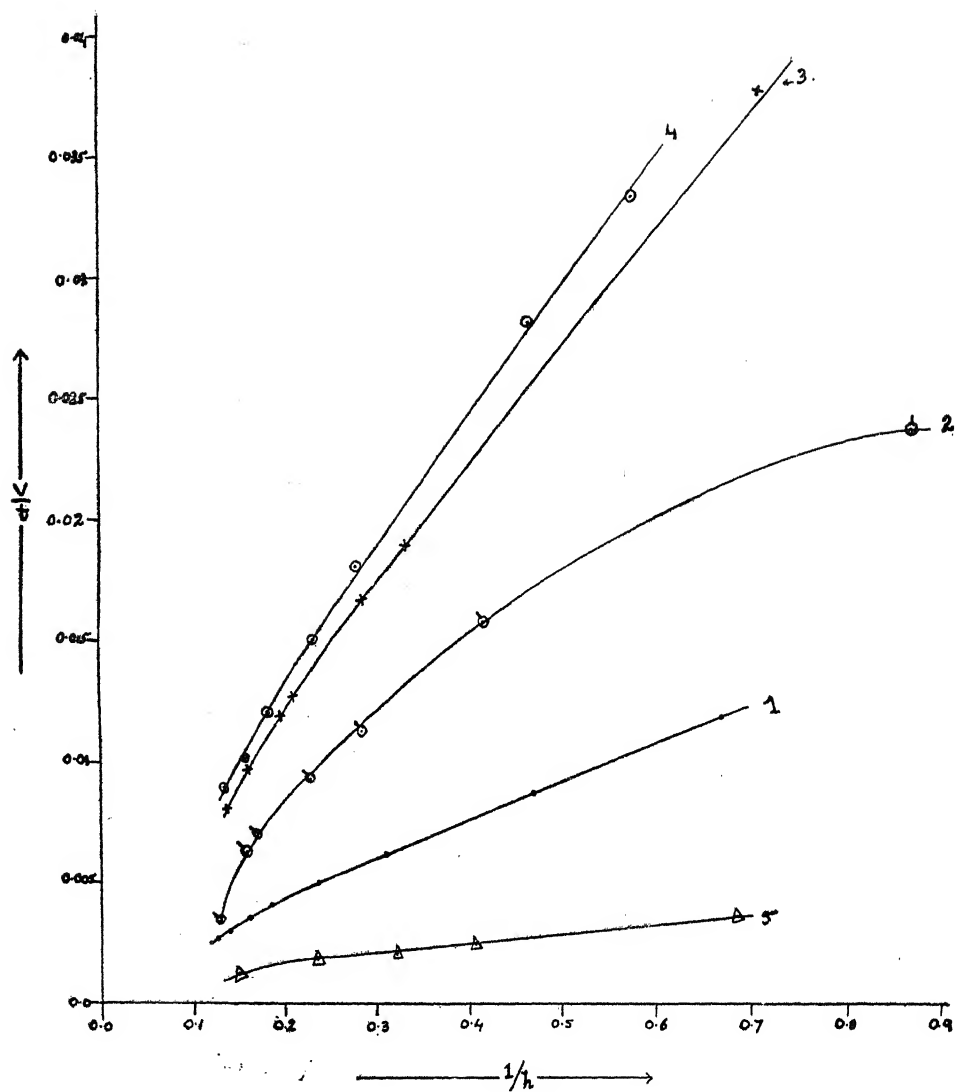
Curve No. 1—Rate of Flow of Water Through Different Heights of Adsorbents.

1. Calcium Carbonate.
2. Silicic Acid.
3. Magnesium Oxide.
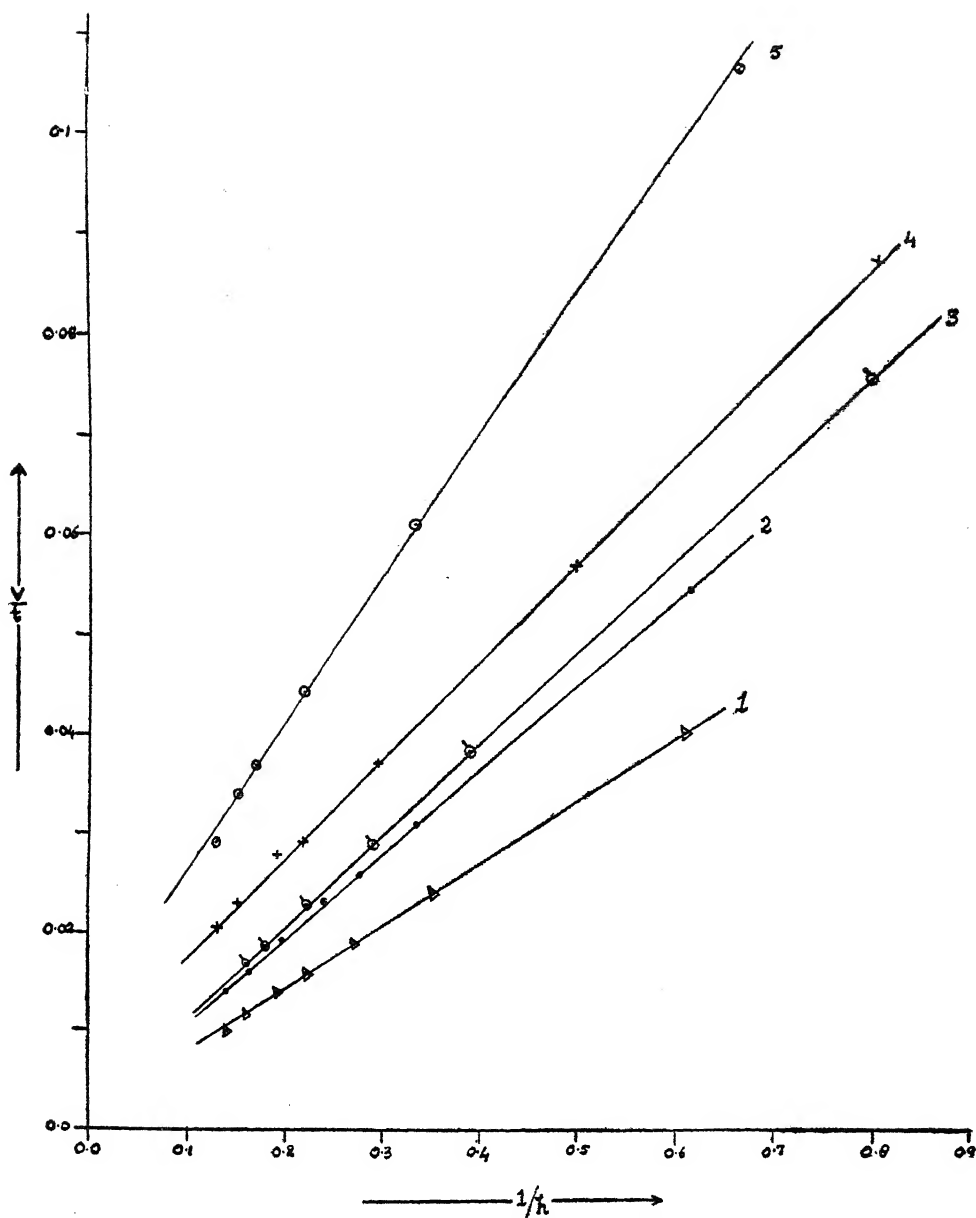4. Kieselgurh.
5. Fuller's earth.
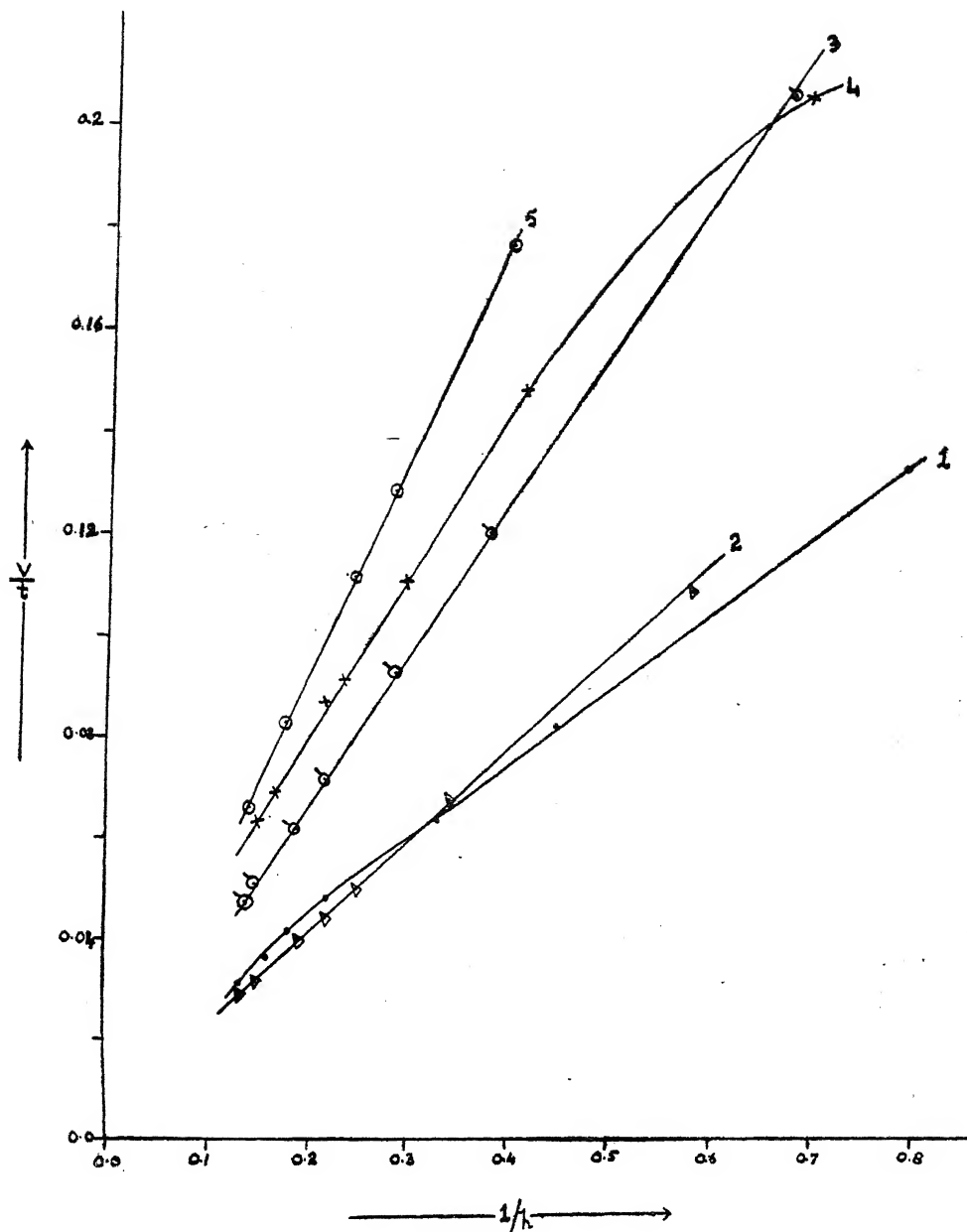
Curve No. 2—Rate of Flow of Methyl Alcohol Through Different Heights of Adsorbents.
1. Fuller's earth.
2. Calcium Corbonate.
3. Silicic Acid.
4. Kieselgurh.
5. Magnesium Oxide

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Curve No. 3.—Rate of Flow of Methyl Acetate Through Different Heights of Alsorbents.

1. Calcium Carbonate.
2. Silicic Acid.
3. Fuller's earth.
4. Kieselgurh.
5. Magnesium Oxide.

Curve No. 4.—Rate of Flow of Acetone Through Different Heights of Adsorbents.

1. Fuller's earth.
2. Calcium Carbonate.
3. Silicic Acid.
4. Kieselgurh.
5. Magnesium Oxide.

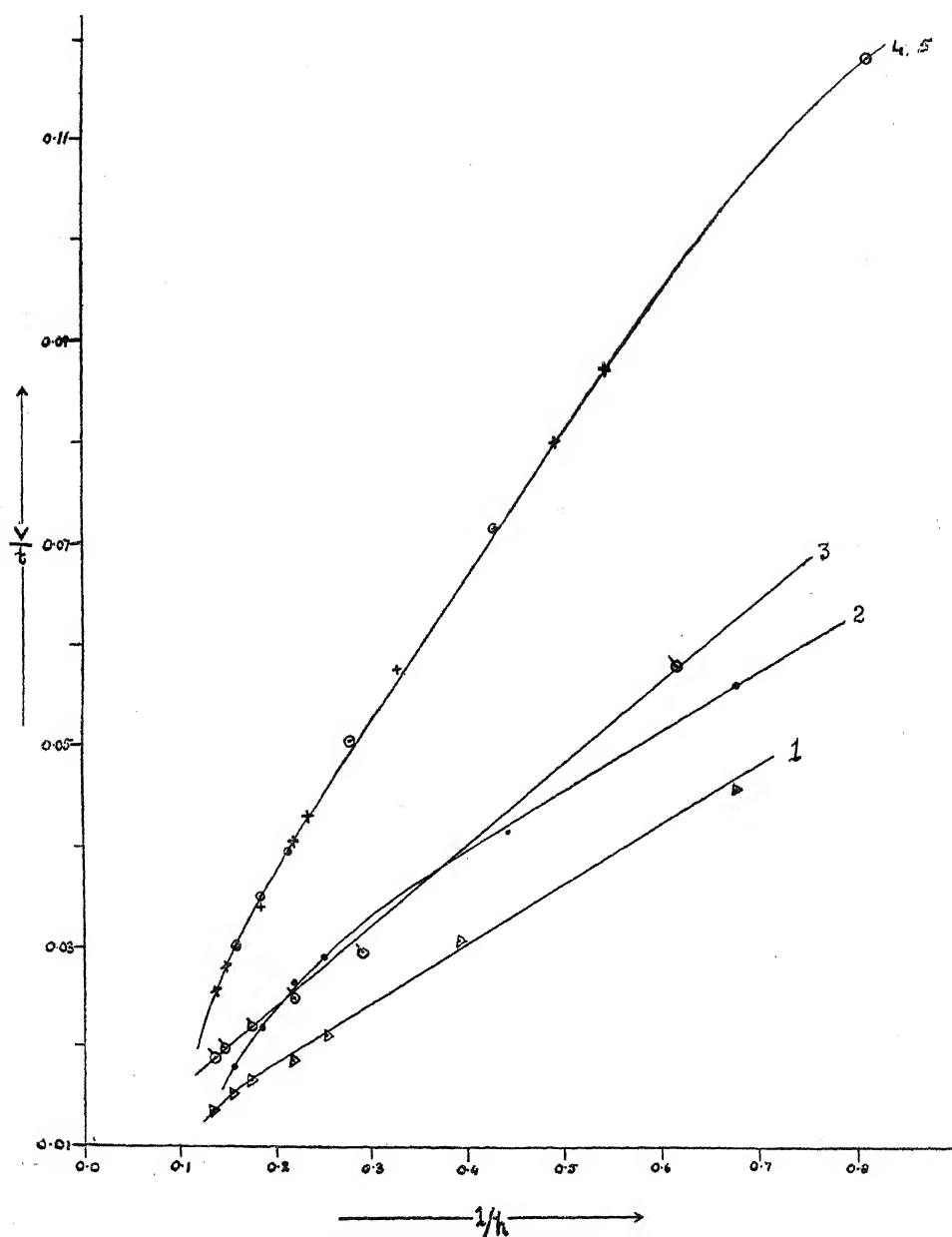Curve No. 5.—Rate of Flow of Benzene Through Different Heights of Adsorbents.

1. Fuller's earth.
2. Silicic Acid.
3. Magnesium Oxide.
4. Kieselgurh.
5. Calcium Carbonate.

DISCUSSION

In curve nos. 1-5, the relation between v/t and $1/h$ has been depicted. It is extremely interesting that the curves are almost linear showing that the velocity of flow is inversely proportional to the height upto an optimum value of h (approximately 4·50 cms.).

The figures obtained for the rate of flow of water when it passed through approximately equal heights of different columns are for calcium carbonate (·0036), silicic acid (·0063), Fuller's earth (·0013), kieselguhr (·0106) and magnesium oxide (·0097). According to these figures the above adsorbents may be arranged in the order of their water transmission capacity as kieselguhr > magnesium oxide > silicic acid > calcium carbonate > Fuller's earth. The similar results are obtained for methyl alcohol, methyl acetate, acetone and benzene where the rate of flow of the liquid and the order of the liquid transmission capacity are found to be specific with the suface properties of the adsorbents and the structure of the liquid. Through the silicic acid and kieselguhr columns the velocity of transmission can be arranged as benzene > methyl acetate > acetone > water > methyl alcohol. This similarity of the order was in all probability due to the geometrically similar pores and passage of the two systems ; or, in other words, this may be ascribed to the supposed similarity of surface characteristics of silicic acid and kieselguhr. The order of flow through calcium carbonate column is benzene > acetone > methyl acetate > water > methyl alcohol, for Fuller's earth, it is methyl acetate > benzene > acetone > methyl alcohol > water ; and, with magnesium oxide, it is methyl acetate > acetone > benzene > water > methyl alcohol. The foregoing orders of liquid transmissions through different adsorbent columns suggest that the pore factors of these adsorbent columns are appreciably affected by the interfacial forces between the adsorbent and the liquid. Benzene has the highest relative flow through silicic acid, kieselguhr, calcium carbonate, but this is not the case with Fuller's earth and magnesium oxide. The order of flow of water and methyl alcohol is similar in silicic acid, kieselguhr, calcium carbonate and magnesium oxide, but it is not so in the case of Fuller's earth. Similar reverses are observed in the relative flow of benzene, methyl acetate and acetone by changing the adsorbent columns. These observations are very pertinent to warrant the fact that the surface and structural characteristics play a very important role in the flow of liquids through these porous columns. Another striking observation is that a non-polar liquid in general could pass through the porous columns more quickly than the polar ones. Benzene, for example, which is non-polar, has a greater rate of flow through the columns of sicic acid, kieselguhr, Fuller's earth calcium carbonate and magnesium oxide than the velocity of transmission of the polar molecules of water and methyl alcohol.

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[47]

AMINO ACID CONTENT OF THE SEEDS OF *LITSEA CONSIMILIS*

By

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ABSTRACT

The seeds of a medicinal plant, *Litsea consimilis*, growing abundantly in Kumaon region have been investigated with a view to determining their amino acid content. Water, 10% NaCl and 0·2% NaOH solutions were employed to isolate the proteins from the seeds which were found to be made up of cystine, histidine, glutamic acid, proline, alanine, tyrosine, valine, phenyl alanine and leucine.

A number of plants growing wildly in Kumaon region have found wide applications in medicine. The medicinal use of different parts *i.e.* roots, bark, leaves and seeds of *Litsea chinensis, Litsea polyantha* and *Litsea stocksii* beloning to *Lauraceae* family has been described.[2] The seeds of *Litsea chinensis* are aphrodisiac, and its seed oil is used in rheumatism. The oil from the seeds of *Litsea stocksii* is used in the treatment of sprains and itch. *Litsea consimilis*, another species of *Lauraceae* has not been examined for its medicinal value. This plant occurs plently in Kumaon region. The oil from its berries is used by the local people in the treatment of various skin diseases and is applied for healing wounds. It was, therefore, considered worthwhile to take up a systematic investigation of the seeds of *Litsea consimilis*. In the present communication, the authors describe the isolation of proteins from the seeds and the characterization of amino acids in the protein hydrolysates by descending paper chromatographic technique. The results of the investigations of the seed oil will be communicated separately.

EXPERIMENTAL

Water, neutral saline solution, 70-80% alcohol, and dilute solutions of acids and alkalis have been commonly employed to isolate proteins from plants and seeds[1,4]. No single solvent was, however, found suitable to isolate completely the protein matter from the seeds of *Litsea consimilis*.

(a) Isolation of protein matter from the seeds :—

The oil from the seeds was removed by refluxing their powder with petroleum ether. The defatted seed powder was treated successively with water, 10% NaCl solution and 0·2% NaOH solution.

35 gms. of the finely powdered material were mixed with 350 ml of distilled water and stirred for about 3 hours and then filtered. The residue (No. 1) was shaken with 200 ml of 10% NaCl solution, stirred for two hours and filtered. The residue (No. 2) was freed from NaCl by washing with distilled water and then stirred with 350 ml of 0·2% NaOH for two hours and finally filtered. The residue (No. 3), after freeing it from NaOH, did not give positive test for nitrogen. Thus the protein matter of the seeds was completely extracted by water, 10% NaCl solution and 0·2% NaOH solution.

The water, 10% NaCl and 0·2% NaOH soluble protein matter was dialysed separately for 4-5 days and the dialysates were evaporated to dryness over water bath. The protein matter obtained from water, 10% NaCl and 0·2% NaOH solutions weighed 1·70, 1·50 and 1·21 gms. respectively.

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(b) Hydrolysis of the protein matter :—

0·2 – 0·5 gm of the material from each extract was separately refluxed with 20 ml of 6 N.HCl for 12 hours on a sand bath. The acid was completely removed from the hydrolysates by treating them in an electrolytic desalting apparatus (Shandon type). Each of the hydrolysates was then extracted with absolute alcohol.

(c) Characterization of amino acids in protein hydrolysates :—

Amino acids were characterized by employing descending paper chromatographic technique as described earlier[3]. 0·004 ml – 0·008 ml of the protein hydrolysates and 0·002 ml of reference amino acids were chromatographed together on Whatman filter paper No. 1 (sheets 48 × 28 cms.). The chromatograms were equibrated with the lower layer of *n*-butanol-acetic acid-water[3] (4:1:5, v/v) for 24 hours and were developed by the upper layer (solvent phase) of the above mixture for 36 hours at the room temperature. The multiple development process was employed with a view to achieving better and distinct separation of amino acids which were located as usual by spraying the chromatograms with a 0·1% solution of ninhydrin in acetone and placing them in an electric oven at 65°C for 10-15 minutes.

The total number of amino acids present in the above three protein fractions were also confirmed by analysing chromatographically a mixture of three hydrolysates taken together.

The amino acids present in the protein fractions isolated from the seeds of *Litsea consimilis* have been given in Table 1.

TABLE 1

Amino-acids present in the protein hydrolysates of the seeds of *Litsea consimilis*

Protein fraction	Amino acids identified
Soluble in water ...	Cystine, glutamic acid, proline alanine, tyrosine, phenyl alanine and leucine.
Soluble in 10% NaCl solution ...	Cystine, glutamic acid, alanine, tyrosine, valine, phenyl alanine and leucine.
Soluble in 0·2% NaOH solution	Histidine, glutamic acid, alanine, tyrosine, valine, phenyl alanine and leucine.
Mixture of the above 3 protein fractions.	Cystine, histidine, glutamic acid, proline, alanine, tyrosine, valine, phenyl alanine and leucine.

The proteins of the seeds of *Litsea consimilis* are, therefore, made up of cystine, histidine, glutamic acid, proline, alanine, tyrosine, valine, phenyl alanine and leucine.

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SALT EFFECT IN THE SILVER CATALYSED OXIDATION OF SODIUM OXALATE BY POTASSIUM PERSULPHATE

By

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ABSTRACT

The study of the salt effect for the silver catalysed oxidation of sodium oxalate by potassium persulphate has been carried out in presence of sodium sulphate and potassium sulphate as neutral salts. In both the cases it is found that the salt effect is negative and of the primary exponential type. Further, the value of $Z_A Z_B$, the product of valencies of the reacting ions in the rate determining process has been calculated, which is found to be 2·49 and 2·45 in case of sodium sulphate and potassium sulphate respectively showing thereby that the rate determining process is probably a reaction between a bivalent and a monovalent ion of opposite charges.

INTRODUCTION

In a previous communication[1], we have presented the results on the salt effect due to potassium and sodium sulphates respectively on the silver catalysed oxidation of oxalic acid by persulphate ion at low ionic strength. It was found that the salt effect was negative and primary exponential in character. Since Gupta and Ghosh,[2,3] in a study of the silver catalysed oxidation of oxalic acid and oxalate ion by persulphate ion had reported that the two reactions are different in behaviour, the oxidation of oxalic acid being characterised by a long induction period, it was considered necessary by us to carry out the study of salt effect on silver catalysed oxidation of oxalate ion by persulphate ion also to find out whether the effect is similar or not and thereby attempt to elucidate the mechanism of this reaction.

In the present paper, the results on the salt effect due to potassium sulphate and sodium sulphate on the silver catalysed oxidation of oxalate ion by persulphate ion have been presented.

EXPERIMENTAL

The experimental technique followed in the study of this reaction is the same as followed by us in the study of silver catalysed oxidation of oxalic acid by persulphate ion (*loc. cit.*).

RESULTS AND DISCUSSION

The study of Gupta and Ghosh (*loc. cit.*) of the silver catalysed oxidation of potassium oxalate by potassium persulphate in presence of a high concentration of sulphuric acid has shown that the reaction is amenable to a definite order under certain conditions. However, our study of the oxalic acid - persulphate reaction (*loc. cit.*) at low concentration had shown that the silver catalysed reaction is autocatalytic just like the uncatalysed reaction studied by Srivastava and Ghosh[4]. We find that the silver catalysed oxidation of sodium oxalate by potassium persulphate is also autocatalytic, as illustrated by the following data.
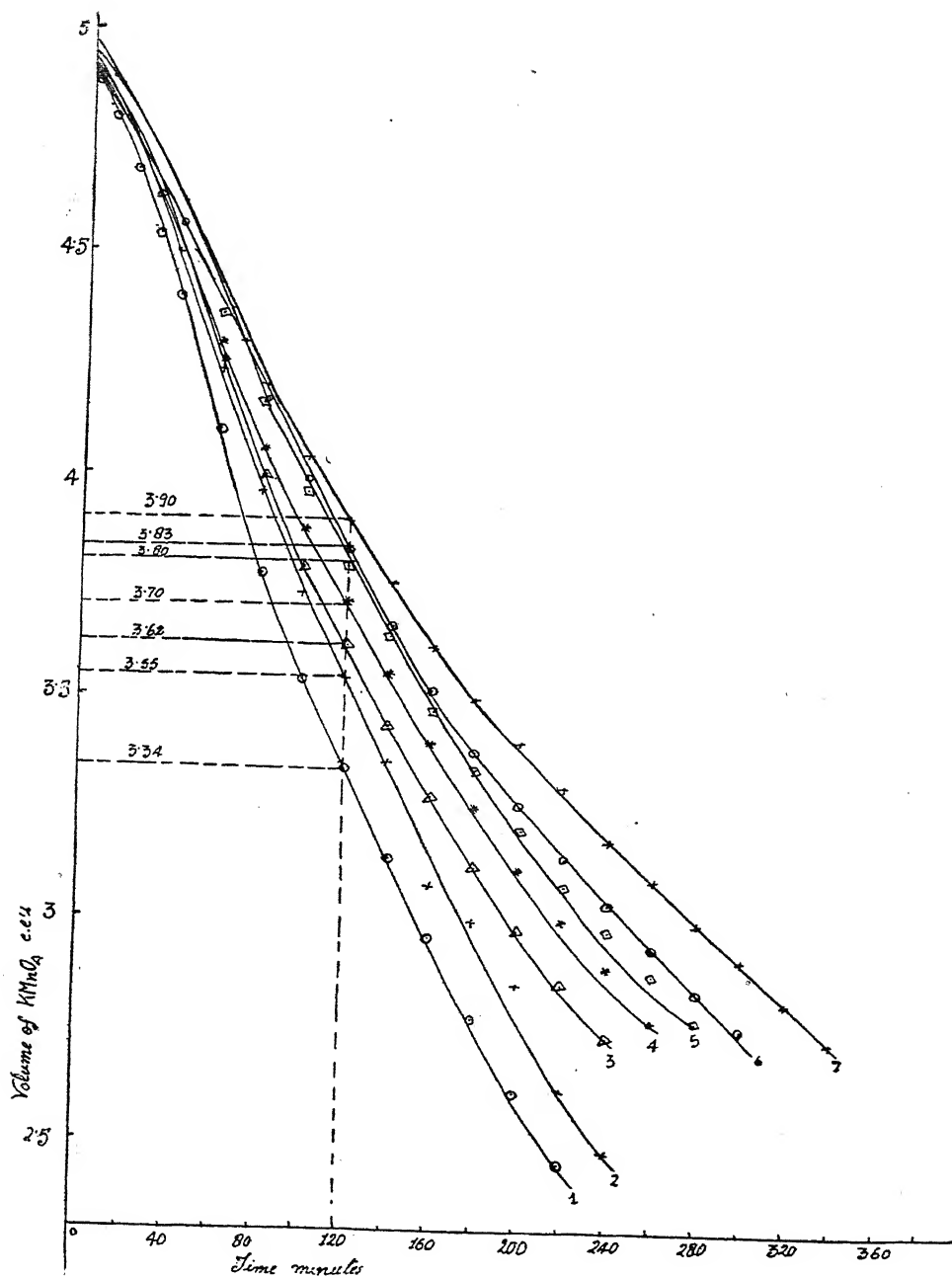
Fig. No. 1. Ag$^+$ Catalysed reduction of $K_2S_2O_8$ at 45°C. $K_2S_2O_8 = Na_2C_2O_4$ $=0\cdot005M$; $AgNO_3=0\cdot0001M$. Na_2SO_4 in (1) $= 0\cdot000M$; in (2)$=0\cdot005M$; in (3)$=0\cdot006M$; in (4)$=0\cdot007M$; in (5)$=0\cdot008M$; in (6)$=0\cdot009M$; in (7)$=0\cdot010M$.

[51]

TABLE I

$K_2S_2O_8 = Na_2C_2O_4 = 0.005$ M, $AgNO_3 = 0.0001$ M, Temp. $45°C$

Time in Minutes	Volume of KMnO₄ (ml.)	$\left(-\dfrac{\Delta c}{\Delta t}\right)$
0	4·88	...
10	4·80	0·0080
20	4·68	0·0100
30	4·54	0·0113
40	4·40	0·0120
60	4·10	0·0130
80	3·78	0·0137
100	3·54	0·0134
120	3·34	0·0128
140	3·14	0·0124
160	2·96	0·0120
180	2·78	0·0116
200	2·62	0·0113
220	2·46	0·0110

The above results clearly show that the reaction is autocatalytic and it is followed by auto-inhibition in the later stages just as in the oxidation of oxalic acid. A comparison with the rate-data for oxalic acid shows that the reaction with oxalate ion is slightly faster than with oxalic acid. However, the nature of reaction remains the same in the two cases, unlike the observation of Gupta and Ghosh, who found that oxalic acid and normal oxalate react differently with persulphate.

Salt Effect.—In the case of silver catalysed oxalic acid - persulphate reaction, we have shown that at low ionic strength a negative exponential salt effect is present. In order to decide whether oxalic acid and oxalate ion react differently with persulphate ion or not, the study of salt effect on silver catalysed oxalate - persulphate reaction at low ionic strength was undertaken by us. Fig. No. 1 represents the effect of various concentrations of added sodium sulphate on the rate of reaction while fig. No. 2 represents the effect due to added potassium sulphate. In each case when the value of $\log x$ (x = amount of sodium oxalate decomposed in 120 minutes) is plotted against $\sqrt{\mu}$, a very closely linear curve is obtained, showing thereby that the negative salt effect is of the primary exponential type, as is also obtained in the reaction with oxalic acid. This shows that the rate determining process is
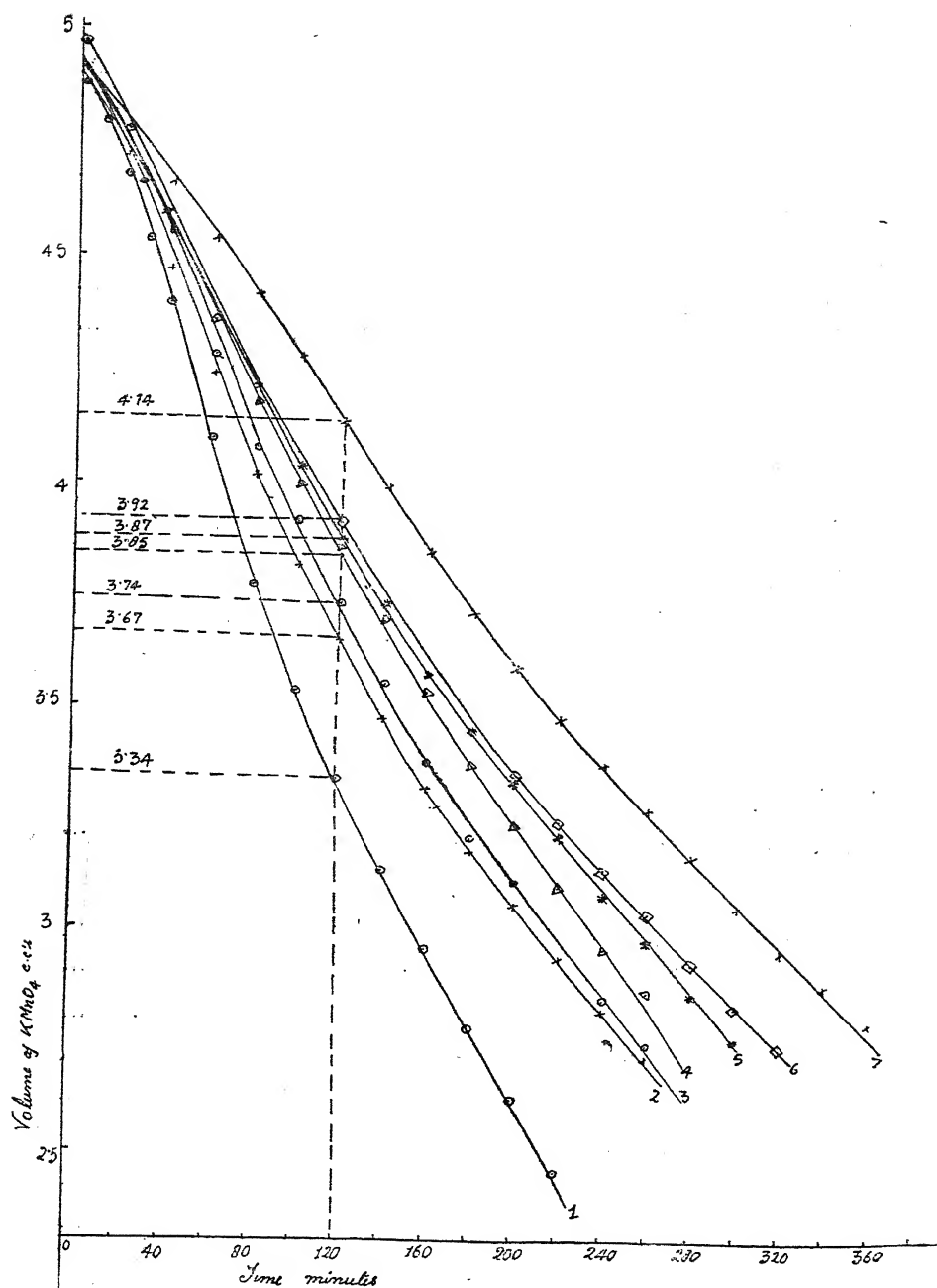
Fig. No. 2. Ag⁺ Catalysed reduction of $K_2S_2O_8$ at 45°C. $K_2S_2O_8 = Na_2C_2O_4$ = 0·005M ; $AgNO_3 = 0·0001M$; K_2SO_4 in (1)=0·00M in (2)=0·005M ; in (3)=0·006M ; in (4)=0·007M ; in (5)=0·008M ; in (6)=0·009M ; in (7) =0·010M.

[53]

between two oppositely charged ions. In order to determine the valency of these oppositely charged ions, the value of constant A in the equation

$$\log k = \log k_0 + 2A Z_A Z_B \sqrt{\mu} \qquad \qquad \dots \ (1)$$

was first calculated by the expression

$$A = \frac{1 \cdot 826 \times 10^6}{(\Sigma\ T)^{3/2}} \qquad \qquad \dots \ (2)$$

where Σ was calculated by the use of the equations

$$\Sigma = 78 \cdot 54\ [1 - 0 \cdot 0046\ (t - 25) + 0 \cdot 0000088\ (t - 25)^2] \qquad \dots \ (3)$$

$$\text{and } \Sigma = 78 \cdot 57\ [1 - 0 \cdot 00461\ (t - 25) + 0 \cdot 0000155\ (t - 25)^2] \qquad \dots \ (4)$$
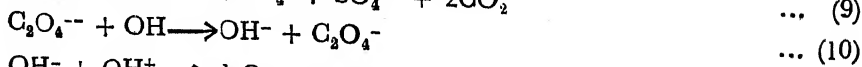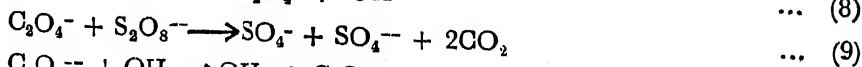
and the mean taken (Kortum and Bockris - Electro - chemistry, Volume I).

The value of A thus calculated comes out to be 0·706. Using this value of A, the value of $Z_A Z_B$ is calculated from the slope of the curves in figs. 1 and 2. The values of $Z_A Z_B$ are 2·49 and 2·45 in the case of sodium sulphate and potassium sulphate as added salts respectively. This firstly shows that the two salts used, *viz.*, sodium sulphate and potassium sulphate have either no specific ionic effect or have similar specific effect and secondly the rate determining process is probably a reaction between a bivalent and a monovalent ion of opposite charges. The slight deviation in the value of $Z_A Z_B$ from 2 may be due to firstly specific effect of ions involved and secondly due to inherent complications in the reaction.

However, since the reaction shows a negative exponential salt effect and the value of $Z_A Z_B$ is nearly 2, it may be assumed that the rate determining process is;

$$S_2O_8^{--} + Ag^+ \longrightarrow SO_4^{--} + SO_4^- + Ag^{++} \qquad \qquad \dots \ (5)$$
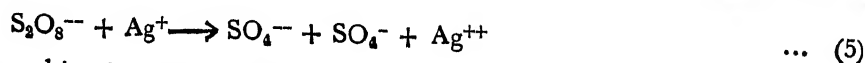
followed by the rapid processes :—

$$SO_4^- + H_2O \longrightarrow HSO_4^- + OH \qquad \qquad \dots \ (6)$$

$$OH + Ag^{++} \longrightarrow Ag^+ + OH^+ \qquad \qquad \dots \ (7)$$

$$OH^+ + C_2O_4^{--} \longrightarrow C_2O_4^- + OH \qquad \qquad \dots \ (8)$$

$$C_2O_4^- + S_2O_8^{--} \longrightarrow SO_4^- + SO_4^{--} + 2CO_2 \qquad \qquad \dots \ (9)$$

$$C_2O_4^{--} + OH \longrightarrow OH^- + C_2O_4^- \qquad \qquad \dots \ (10)$$

$$OH^- + OH^+ \longrightarrow \tfrac{1}{2} O_2 + H_2O \qquad \qquad \dots \ (11)$$

$$O_2 + C_2O_4^- \longrightarrow 2CO_2 + O_2^- \qquad \qquad \dots \ (12)$$

$$O_2^- + SO_4^- \longrightarrow O_2 + SO_4^{--} \qquad \qquad \dots \ (13)$$

The above scheme is similar to the scheme proposed by Bhakuni and Srivastava[5] for the silver catalysed oxidation of oxalic acid by persulphate ion. The autocatalysis is explained by the fact that $C_2O_4^-$ produced in (8) is also responsible for the production of the active ion SO_4^-. The auto-inhibition in the later stages is accounted for by the removal of the active species $C_2O_4^-$ and SO_4^- by interaction with oxygen.

The slight increase in reaction rate in the case of oxalate-persulphate reaction in comparison to that of oxalic acid - persulphate reaction may be due to the slight difference in the active concentration of $C_2O_4^{--}$ in the two cases due to incomplete dissociation of oxalic acid.

ACKNOWLEDGMENT

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CHEMICAL EXAMINATION OF *MIMUSOPS ELENGI*, LINN. PART I

EXAMINATION OF THE FATTY OIL FROM THE SEEDS

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The component fatty acids of the seed fat of *Mimusops Elengi*, Linn. have been found to be capric, lauric, myristic, palmitic, stearic, archidic, oleic and linoleic acids. The un-saponifiable matter of the oil consisted of β and γ-sitosterols.

Mimusops Elengi. Linn. (N. O. Sapotaceae) commonly known as Sinhakesara or Bakula in Sanskrit and Maulsiri in Hindi is a large ornamental trees cultivated in gardens for its fragrant flowers. The bark, flowers, fruit and seeds of this tree find use in the indigenous system of medicine. The seeds are said to be purgative in its action[1]. The seeds contain 13·6% oil. The seed fat was first examined by Rau and Simonsen[2] who resolved it into four fractions by a simple form of the fractional distillation procedure and later by Kartha and Menon[3] who used a more elaborate form of the technique and separated five component fatty acids, palmitic, stearic, archidic, oleic and linoleic in 11·0, 10·1, 0·4, 64·0 and 14·5% yields respectively. The earlier analyses gave less detailed information and in view of the medicinal use of the various parts of this tree, a systematic chemical examination has been undertaken and the examination of the fatty oil from the seeds has been described in this communication.

The seeds of *Mimusops elengi*, linn. furnished on extraction with petroleum ether (b. p. 40º — 60°), an yellow coloured oil in 13·6% yield. The crude oil was purified by repeated treatment with animal charcoal and Fuller's earth when a bright coloured yellow oil possessing the following characteristics was obtained.

Specific gravity at 25°	... ...	0·9302
Refractive index at 25°	... ...	1·4676
Acid value	... ...	11·4500
Acetyl value	... ...	17·4650
Saponification value	... ...	245·7500
Iodine value (Hanus)	... ...	63.5000
R. M. value	... ...	2·0000
Hehner number	... ...	92·9500
Unsaponifiable matter	... ...	1·6000 percent.

The oil was saponified with alcoholic potassium hydroxide and the resulting soap solution was extracted with ether to remove the unsaponifiable matter. The fatty acids were liberated by treatment of the soap with dil. sulphuric acid. The oil contained some proportion of saturated acids of lower molecular weight together with a large proportion of unsaturated acids. The acids were not separated into

solid and liquid acids by the usual procedure but instead, the acids were first esterified together by the method of Hilditch[4]. The mixed acids possessed the following characteristics :

Iodine value	... ...	63·80
Saponification value	... ...	260·40

The lower saturated esters (upto C_{14}) were separated by fractional distillation and the residual esters after hydrolysis were treated with Twitchell lead salt alcohol method of separation as modified by Hilditch[5]. The solid and liquid acids so obtained were re-esterified and further separated by fractionation in vacuum. The saponification value of each fraction was determined and the composition of each fraction was found out. The results are recorded in Table 1.

TABLE 1

Fractional distillation of saturated methyl esters upto C_{16} acids

Praction No.	Weight in g.	b. p./15 mm. in °C	S. V.	C_8 in g.	C_{10} in g.	C_{12} in g.	C_{14} in g.	C_{16} in g.
1	0·55	90-100	161·2	0·05	0·50	...	...	...
2	2·48	100-120	178·8	...	2·46	0·02	...	...
3	0·84	120-130	180·0	...	0·36	0·48	...	...
4	8·77	130-131	195·2	...	...	8·52	0·25	...
5	4·71	131-135	198·5	...	...	4·26	0·45	...
6	2·44	136-140	199·8	...	...	0·24	2·20	...
7	7·20	140-141	200·0	...	...	...	0·34	6·86
8	17·24	141-145	216·0	...	...	...	...	17·24
9	39·74	146-150	220·5	...	...	...	...	39·74
10	Residual extracts were not distilled further							
Total	83·97	total distillate		0·05	3·32	13·52	3·24	63·84

Identification of the solid acids :—The various ester fractions indicated in Table 1 were saponified separately and the corresponding acids were examined. Fraction 1 yielded liquid acid of mean M. W. 168, indicating the presence of capric acid which was subsequently confirmed by preparing its anilide derivative (m. p. 74°) and by observing its m. p. and mixed m. p. of the anilide obtained from an authentic

[57]

specimen of capric acid when no depression in m. p. was noted. Fraction 2 yielded acids with a mean M. W. 185·0. The acids of this fraction were separated by fractional distillation and the fraction distilling at 267° – 269° was collected separately. This fraction was found to have M. W. 172 conforming to that of capric acid. The presence of capric acid in this fraction was also confirmed by preparing its anilide derivative and observing the m. p. and mixed m. p. with an authentic specimen. The residual acid in fraction 2 was identified as lauric acid (m. p. 44°) and was confirmed by observing the m. p. and mixed m. p. with an authentic specimen when no depression in m. p. was noted. Fraction 3 and 4 also yielded capric and lauric acids while fraction 5, 6 and 7 contained lauric acid alone.

Fraction 8 yielded acids of mean M. W. 224. On fractionation, this fraction yielded two acids, lauric and myristic. The presence of lauric acid was confirmed in the manner stated above by preparing its anilide derivative. The presence of myristic acid (M. W. 228) was also confirmed by preparing its anilide (m. p. 84°) and observing the m. p. and mixed m. p. with an authentic specimen when no depression in m. p. was noted. The presence of palmitic acid in fraction 9 was confirmed in the usual manner.

The mixed acids obtained on hydrolysis of the residual esters possessed the following characteristics :

Specific gravity at 25°	...	...	0·9302
Saponification value	...	...	278·5000
Iodine value	...	...	24·0000

The acids, separated into solid and liquid acids by Twitchell's lead salt alcohol method as modified by Hilditch[5] possessed the following characteristics :

TABLE 2

Characteristics of the liberated acids

Serial No.	Acids	Yield in percent	Iodine value	Molecular Weight
1	Solid acids	27·99	1·25	272·6
1	Liquid acids	72·01	90·95	280·2

The liberated acids were re-esterified and the esters obtained were fractionated in vacuum. The saponification value and other properties of each fraction of the methyl esters of solid acids were determined and have been shown in Table 3.

TABLE 3

Fractionation of residual esters of higher saturated esters

Fraction No.	Wt. in g.	b. p./15 mm. in °C	Iodine value	Saponification value	Palmitic	Stearic	Archidic	Unsaturated
1	9·407	200-205	2·56	286·4	0·358	1·560	0·025	7·364
2	12·098	above 205 (residue)	2·60	287·5	1·085	0·628	0·400	10·085
Total	21·505	...	...	...	1·443	2·188	0·425	17·449

TABLE 4

Fractionation of the liquid esters

Fraction No.	Weight in g.	b. p./15 mm. in degrees C.	Iodine value	Saponification value	Oleic	Linoleic
1	16·330	215-216	86·6	296·2	16·246	0·C84
2	6·212	above 216	87·5	297·0	2·050	4·162
Total	22·542	...	...	...	18·296	4·246

The presence of oleic acid was confirmed by hydrolysing the ester and oxidising the resulting acid with dil. alkaline potassium permanganate when dihydroxystearic acid (m. p. 134°) was obtained ; and linoleic acid by adding bromine when crystalline tetrabromostearic acid (m. p. 115°) was obtained.

The unsaponifiable matter obtained from the seed fat of *Mimusops elengi*, linn. consisted of β and γ-sitosterols.

SUMMARY

On analysis, the fatty oil from the seeds of *Mimusops elengi*, Linn. was found to contain the following component fatty acids :

Capric acid	--- 1·10	percent
Lauric acid	... 3·38	,,
Myristic acid	... 1·08	,,
Palmitic acid	... 11·04	.,
Stearic acid	... 11·35	,,
Arehidic acid	--- 0·55	,,
Oleic acid	--- 58·44	,,
Linoleic acid	... 13·06	,,

The unsaponifiable matter from the seed fat consisted of β and γ sitosterols.

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KINETICS OF OXIDATION OF FORMALDEHYDE IN AQUEOUS SOLUTION BY POTASSIUM PERSULPHATE—PART I*

By

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INTRODUCTION

During the course of our kinetic study of the oxidation of acetone and other ketones by persulphate ion,[1] we found that aldehydes are also oxidised by persulphate ion in presence of $AgNO_3$ as catalyst. With a view to determine the exact nature of stages of the oxidation of ketones and aldehydes, the present study on the oxidation of formaldehyde by persulphate ion was carried out. Inspite of a large amount of work on the kinetics of oxidation by persulphate ion, very little work seems to have been carried out on the oxidation of organic compounds by persulphate ion with the aim of determining the different stages of oxidation of organic compounds. It may be pointed out that persulphate ion being a milder oxidising agent than permanganate ion or dichromate ion is more suitable for this purpose. Mention may be made of the previous study of oxidation of hydrazine,[2] alkyl iodides[3] and of acetone[4] by persulphate ion.

EXPERIMENTAL

Formaldehyde and potassium persulphate used were of G. R. E. Merck grade and the other salts used were of A. R. B. D. H. quality. The standard solution of formaldehyde was prepared by iodometric estimation while the standard solution of potassium persulphate was prepared by direct weighing of the salt and the strength of the solution was checked by iodometric estimation as followed in our work on the oxidation of acetone by persulphate ion (loc. cit). A freshly prepared solution of potassium persulphate was always used. The experimental technique followed in this investigation was the same as followed in our study of acetone reaction and the reaction was always carried out in the dark. The progress of the reaction was followed by estimating the unreacted potassium persulphate by iodometric method at different intervals of time. Blank titrations of potassium persulphate in presence of formaldehyde were first of all carried out to find whether the presence of formaldehyde affects this method of estimation of potassium persulphate or not. These experiments showed that no appreciable error was caused by the presence of formaldehyde in this method of estimation.

RESULTS OF MEASUREMENTS

First of all the uncatalysed oxidation of formaldehyde by potassium persulphate was carried out at 45°C., the results of which are recorded below:

TABLE I

Reaction mixture.
HCHO
$K_2S_2O_8$

Temperature. 45°C
Overall concentration.
0·8%
0·04 M.

Time in minutes	Volume of N/50 $Na_2S_2O_3$ in c.c.	Volume of $Na_2S_2O_3$ corresponding to $K_2S_2O_8$ conc.	$k \times 10^3$ (Unimolecular)
0	21·41	19·41	...
10	21·36	19·36	0·2533
30	21·29	19·29	0·2149
60	21·09	19·09	0·2801*
90	21·30	19·00	0·2354
120	20·76	18·76	0·2840*
150	20·67	18·67	0·2594
180	20·52	18·52	0·2554
210	20·45	18·45	0·2423
240	20·33	18·33	0·2338
270	20·23	18·23	0·2320
300	20·12	18·12	0·2295
360	19·93	17·93	0·2194
	Mean		0·2449

It is seen that the uncatalysed reaction is very slow, about 1/10th of the reaction taking place in six hours. Further, it is seen that the reaction follows an unimolecular behaviour. However, the unimolecular constant has a slight tendency to decrease during the later stages. Since the uncatalysed reaction is very slow even at 45°C., subsequent study was carried out in the presence of $AgNO_3$ as catalyst.

The following table gives the results obtained for the Ag catalysed reaction at 35°C.

TABLE II

Reaction mixture		Temperature 35°C
		Overall Concentration.
HCHO		0·8 %
AgNO$_3$		0·0001 M
K$_2$S$_2$O$_8$		0·01 M.

Time in minutes	Volume of N/100 Na$_2$S$_2$O$_3$ in c. c.	Volume of Na$_2$S$_2$O$_3$ corresponding to K$_2$S$_2$O$_8$ conc.	$k \times 10^3$ (Unimolecular)
0	24·00	20·00	
30	22·71	18·71	
60	21·64	17·64	2·0918
90	20·58	16·58	2·0829
120	19·65	15·65	2·0439
150	18·65	14·65	2·0757
180	17·90	13·90	2·0215
210	17·20	13·20	1·9783
240	16·77	12·77	1·8651
270	16·03	12·03	1·8704
300	15·43	11·43	1·8654
330	14·62	10·62	1·9183
360	14·10	10·10	1·8980
390	13·64	9·64	1·8354
		Mean	1·9620

It will be seen that the Ag$^+$ catalysed reaction is also unimolecular and has a measurable rate at 35°C. Since the formaldehyde concentration has been taken in excess, this also indicate that the order of reaction with respect to K$_2$S$_2$O$_8$ is one.

EFFECT OF POTASSIUM PERSULPHATE CONCENTRATION

In order to determine the effect of K$_2$S$_2$O$_8$ concentration on the rate, the reaction was carried out at different initial concentrations of K$_2$S$_2$O$_8$, the results of which are summarised below :—

TABLE III

HCHO = 0·8 %, AgNO$_3$ = 0·0001 M. Temperature 35°C

Conc of K$_2$S$_2$O$_8$	$k \times 10^3$ (Unimolecular)
0·010 M	1·9620
0·015 M	2·0358
0·020 M	2·1221
0·025 M	2·4301
0·030 M	2·8128

At all these concentrations of K$_2$S$_2$O$_8$ it is found that the overall order of the reaction remains one and the rate constant increases with an increase in the initial concentration of K$_2$S$_2$O$_8$. However, no linear relationship between K$_2$S$_2$O$_8$ concentration and the rate constant is obtained ; which indicates that the reaction is probably attended with complications.

Effect of AgNO$_3$ Concentration—The following table summarises the results obtained at various concentrations of the catalyst AgNO$_3$.

TABLE IV

HCHO = 0·8 %, K$_2$S$_2$O$_8$ = 0·01 M. Temperature 35°C.

Conc of AgNO$_3$	$k \times 10^3$ (Unimolecular)
0·0001 M	1·9620
0·0002 M	2·7527
0·0003 M	4·0141
0·0004 M	5·3666
0·0005 M	6·3058

When a graph is plotted between the concentration of AgNO$_3$ and the rate constant a linear curve is obtained, indicating that the rate is linearly related to the AgNO$_3$ concentration, that is, $dx/dt \propto C_{Ag^+}$.

[63]

In order to determine the role of formaldehyde concentration on the rate the reaction was studied at different initial concentrations of formaldehyde keeping the concentration of $K_2S_2O_8$ and $AgNO_3$ the same in different experiments. This study revealed that the results are generally not reproducible. The following table summarises the results obtained in different set of experiments at the same initial concentration of HCHO.

TABLE V

HCHO = 0·01 M, $K_2S_2O_8$ = 0·01 M, $AgNO_3$ = 0·0002 M, Temp. = 35°C

Experiment No.	$k \times 10^3$ (Unimolecular)
I	6·2201
II	3·4281
III	4·4622
IV	3·5202
V	3·7985

An examination of the above results shows that there is a large variation in the k values in different experiments. However, it is seen that in each case there is an approximate constancy in the first order with a slight tendency to decrease in the later stages. Thus the results although not reproducible lead to the conclusion that the overall order of the reaction is unity. However, when the reaction was studied with the same set of solutions on the same day the results were found to be fairly reproducible as indicated by the following set of data.

TABLE VI

HCHO = 0·01 M, $AgNO_3$ = 0·0002 M, $K_2S_2O_8$ = 0·01 M, Temp. 35°C

Time in minutes.	$k \times 10^3$ (Unimolecular)	
	1st Set	2nd Set.
15	5·1433	5·1433
30	5·6268	5·2431
45	5·6449	5·1022
60	5·6192	5·1894
90	5·6577	5·1432
120	5·5003	4·9975
150	5·3414	4·9222
180	5·1395	4·8094
Mean	5·5042	5·0688

In view of the non-reproducible results obtained therein the subsequent experiments were carried out with freshly prepared solution. It will be further seen that the rate constant has increased with a decrease in HCHO concentration (c. f. the effect of HCOOK concentration on the rate in HCOOK-$K_2S_2O_8$ reaction studied by Srivastava and Ghosh).[5]

EFFECT OF TEMPERATURE

In order to determine the temperature coefficient and energy of activation the reaction was carried out at different temperatures from 25°C to 45°C, the results of which are recorded below :—

TABLE VII

HCHO = 0·8 %, AgNO$_3$ = 0·0003 M, $K_2S_2O_8$ = 0·01 M.

Temperature °C.	$k \times 10^3$ (Unimolecular)	Temp. Coefficient
25	1·9177	$Q_{35-25} = 2·08$
30	2·7765	
35	4·0141	$Q_{30-40} = 2·04$
40	5·6671	
45	7·5028	$Q_{45-35} = 1·86$
Mean		1·99

The energy of activation comes out to be 13103 cals. The frequency factor and the entropy of activation between this temperature range are calculated which are tabulated below :—

TABLE VIII

Temperature	Frequency Factor (in litre mols sec^{-1})	Entropy of activation, $\triangle$s (E. U.)
298°K	1·277 × 10^5	− 35·21
303°K	1·283 × 10^5	− 35·22
308°K	1·301 × 10^5	− 35·22
313°K	1·361 × 10^5	− 36·05
318°K	1·243 × 10^5	− 35·18
Mean		− 35·17

A large negative value of entropy of activation suggests that the rate determining stage is probably either between two oppositely charged ions or between an ion and a neutral molecule.

Catalytic Effect of CuSO₄. Persulphate oxidation reactions are known to be generally catalysed by Cu^{++} ions, hence their effect was investigated in this reaction also. The results in the following table show the catalytic effect of Cu^{++} ions.

TABLE IX

$HCHO = 0.01$ M, $K_2S_2O_8 = 0.01$ M, $CuSO_4 = 0.0005$ M, Temp. 35°C.

Time in minutes	Volume of N/100 $Na_2S_2O_3$ in c. c.	Volume of $Na_2S_2O_3$ corresponding to $K_2S_2O_8$ conc.	$k \times 10^3$ (Unimolecular)
0	23·95	19·95	...
15	23·75	19·75	0·6755
30	23·46	19·46	0·8366*
60	23·16	19·16	0·6793
90	22·84	18·84	0·6371
120	22·53	18·53	0·6160
150	22·16	18·16	0·6212
180	21·90	17·90	0·6026
240	21·55	17·55	0·5391
300	21·00	17·00	0·5341
360	20·52	16·52	0·5223
		Mean	0·6056

It is seen that Cu^{++} ions catalyse the oxidation of HCHO by persulphate ion but their catalytic effect is much less than that of Ag^+ ions.

Effect of H₂SO₄. The effect of addition of H_2SO_4 on the Ag^+ catalysed reaction was investigated, the results of which are recorded below :—

[66]

TABLE X

HCHO = 0·01 M, AgNO$_3$ = 0·0002 M, K$_2$S$_2$O$_8$ 0·01 M, H$_2$SO$_4$ = 0·01 M, Temperature 35°C.

Time in minutes	Volume of N/100 Na$_2$S$_2$O$_3$ in c. c.	Volume of Na$_2$S$_2$O$_3$ corresponding to K$_2$S$_2$O$_8$ conc.	$k \times 10^3$ (Unimolecular)
0	23·55	19·55	
15	22·98	18·98	2·0318*
30	22·18	18·18	2·4258*
60	21·37	17·37	1·9729
90	20·52	16·52	1·8705
120	19·70	15·70	1·8266
150	18·81	14·81	1·8500
180	18·12	14·12	1·8078
210	17·51	13·51	1·7601
240	16·90	12·90	1·7321
300	15·70	11·70	1·7112
360	14·61	10·61	1·7000
		Mean	1·8034

It is seen that the addition of H$_2$SO$_4$ and thereby changing the pH of the solution has an appreciable effect on the rate of the Ag$^+$ catalysed reaction, the rate having gone down considerably by the addition of H$_2$SO$_4$.

EFFECT OF SALT CONCENTRATION

The effect of variation of salt concentration on the rate of reaction was investigated by adding different concentrations of K$_2$SO$_4$ solution to the reaction mixture. The results of these experiments are summarised in the following table.

TABLE XI

HCHO = 0·01 M., AgNO$_3$ = 0·0002 M, K$_2$S$_2$O$_8$ = 0·01 M, temperature 35°C

Conc. of K$_2$SO$_4$	μ	$(\mu)^{1/2}$	$k \times 10^3$ (Unimolecular)	log k
0·010M	0·060	0·244	5·4854	− 2·2608
0·020M	0·090	0·300	4·9449	− 2·3059
0·025M	0·105	0·324	3·2591	− 2·4869
0·030M	0·120	0·346	2·6306	− 2·5800

An examination of the above data shows beyond doubt that the rate decreases with an increase in the ionic strength of the medium. However, no quantitative relationship between the rate constant and the ionic strength μ could be established.

Further work on this reaction to determine the nature of the products formed and stages of formaldehyde oxidation is in progress.

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SEMI-MICRO DETERMINATION OF THE NEUTRALIZATION EQUIVA-
LENTS OF HIGHER FATTY ACIDS

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ABSTRACT

Two methods for the semi-microdetermination of the neutralization equivalents of higher fatty acids-one by direct titration with standard alkali and the other by refluxing with an excess of standard alkali and back titrating the excess with standard acid have been described. The indicator employed for the titration, consists of a mixture of phenol red, cresol red and bromothymol blue which gives a sharp end point even in solutions which are coloured due to the solution of fatty acids in alcohol in presence of alkali.

While working on the fatty acid composition of the liver fat from the fish Labeo rohita, a difficulty was experienced in the macro determination of the neutralisation equivalents of those fatty acid fractions which were obtained in low yield. In the present paper two methods - one by direct titration of the fatty acids with standard alkali and the other by refluxing a known weight of the acid with excess of standard alkali and back titrating the excess alkali with standard acid have been employed and it has been found that the latter method gives better results.

Gorbach[1] modified the procedure for the determination of the saponification value on the macroscale for small amounts of original sample. Stetten and Grail[2] used 8 to 20 mg. of the fatty acids, dissolved them in 90% methanol and titrated against 0·16N alkali in 90% methanol using α-naphtholphthalein as indicator. In the methods described by previous workers, the observation of the end point is vitiated in the case of higher fatty acids because of the development of a colour due to the solution of higher fatty acids in ethanol, which increases in intensity with the addition of alkali and heating the mixture. The procedure described below has been found to give very satisfactory results in the above determinations by using a mixture of indicators which was used earlier by Hinton[3] for coloured solutions and we have found that this mixed indicator works very satisfactorily in the case of higher fatty acids.

TABLE I

Direct titration

Acid	Neutralization Equivalent				
	Calculated	Found			
Lauric	200·0	200·8	198·7	197·6	199·2
Myristic	228·0	231·1	230·7	229·4	229·6
Palmitic	256·0	256·4	257·7	254·1	253·6
Elaidic	282·0	284·1	286·4	285·2	283·6
Oleic	282·0	281·4	283·3	282·9	281·6
Linoleic	280·0	279·4	282·4	280·8	281·7

TABLE II

By refluxing with an excess of the alkali and determining the excess
by back titration against standard acid

Acid	Neutralization Equivalent				
	Calculated	Found			
Lauric	200·0	199·5	199·4	200·1	198·8
Myristic	228·0	228·9	287·6	229·3	
Palmitic	256·0	255·7	255·7	257·3	258·1
Elaidic	282·0	283·4	282·9	284·3	282·8
Oleic	282·0	281·9	282·6	284·1	284·6
Linoleic	280·0	283·4	284·1	280·7	283·5

EXPERIMENTAL

Reagents

Standard Oxalic acid solution

0·04N solution of the A.R. oxalic acid was prepared in distilled water freed from carbon dioxide by boiling.

Ethanolic potassium hydroxide

Approximately 0·04N potassium hydroxide solution was prepared in ethanol.

Standard acid solution

Approximately 0·04N solution of A.R. hydrochloric acid in distilled water was employed.

Indicator

0·4% ethanolic solutions of phenol red, bromothymol blue and cresol red were prepared and a mixture of the three in the ratio of 3:1:1 was employed.

Procedure

1. Direct titration

About 50 mg. of the pure and the dried acid sample was weighed in a pyrex glass shell vial and the vial along with the sample was carefully transferred to a Jena glass 100 ml conical flask. 10 to 15 ml of 95% neutral ethanol was added and the flask shaken to bring the sample in solution. 2 to 3 drops of the mixed indicator solution were added and the alkali solution was run in from a burette till the yellow colour changes to pink-violet colour. In the course of titration, the solution in the flack was stirred using a magnetic stirrer. A blank was run simultaneously using all the reagents except the substance.

2. Refluxing about 50 mg. of the fatty acid with about 0·04N ethanolic potassium hydroxide and back titrating the excess alkali with standard (about 0·04N) hydrochloric acid.

About 50 mg. of the fatty acid sample were weighed in a pyrex glass shell vial and the vial along with its contents was carefully transferred to a 100 ml Jena glass conical flask fitted with a B_{10} joint. 2 boiling stones and 10 ml of ethanolic potassium hydroxide solution were added and the contents refluxed over a steam bath for 30 minutes, using a one metre long and 8 mm in diameter Jena glass tube fitted with a B_{19} cone as air condenser. After cooling, the air condenser and the sides of the flask were carefully rinsed with 5 ml neutral ethanol. Three drops of the mixed indicator were added and the excess alkali titrated against 0·04N hydrochloric acid solution till the violet colour changed to yellow. In the course of the titration the stirring was done with a magnetic stirrer. A blank was run simultaneously using all the reagents except the substance.

ACKNOWLEDGMENT

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A STUDY OF THE INHIBITORY INFLUENCE OF Ag+, Au+++, AND Cu++ IONS ON THE DECOMPOSITION OF UREA BY SOYABEAN (GLYCINE SOJA) UREASE

By

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ABSTRACT

The present investigation deals with a study of the inhibitory influence of Ag+, Au+++, and Cu++ ions on the decomposition of urea by soyabean urease at pH 6·8, 7·8 and 8·8. Silver ions have been found to be the greatest inhibitors and the gold ions come in the least ; copper ions come in between the two. The Inhibition in all the cases increases with the concentration of the respective ions and has been found to be maximum at pH 6·8.

INTRODUCTION

The inhibition of the enzymic activity of urease by a large number of substances has been reported in literature. Metallic ions have usually acted as inhibitors. The influence of a large number of metals e. g. As, Se, Sb, Mn, Sn, Pb, Cd, Fe, Bi, Zn, Mg, Te, Hg, Co, Cu, and Ag was studied by A. J. J. Vande Velde.[1] He found that certain elements like S, Se, As, Sb, Mn, and Sn showed scarcely any effect on the decomposition of urea by urease obtained from soyabean meal. Pb, Cd, Fe, Bi and Zn were found to be clearly toxic and Ni, Mg, Te, Hg, Co, Cu, and Ag were found to be strong inhibitors. Rukhelman[2] reported that lead acted as an activator in a quantity of 50-350 mgms. Silver ions were found to be strong inhibitors in citrate buffer at pH 5·6 by Kistiakowsky and collaborators.[3]

In the present investigation, the influence of Ag+, Au+++, and Cu++ ions on the decomposition of urea by soyabean urease, in phosphate buffer, and at pH 6·8, 7·8 and 8·8 has been studied. Silver nitrate, gold chloride and copper sulphate solutions have been taken to study the influence of Ag+, Au+++, and Cu++ ions respectively.

EXPERIMENTAL

The following solutions were used.

Urea solution. A 4·0% solution of urea (A.R. B.D.H.) in distilled water, has been used.

Soyabean powder extract. A 2·0% suspension of soyabean (Glycine soja beans) powder (obtained by grinding soyabean seeds) in distilled water was prepared. It was stirred for fifteen minutes and then allowed to settle. The supernatant liquid was filtered through glass wool and the filtrate was used.

Silver nitrate solutions. The solutions of silver nitrate were prepared by dissolving the requisite amounts of silver nitrate (Johnson, double crystallised) in distilled water.

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Gold Chloride solutons. They were prepared by dissolving the requisite amounts of gold chloride (Johnson and Mathey) in distilled water.

Copper Sulphate solutions. They were prepared by dissolving the requisite amounts of copper sulphate ($CuSO_4$. $5H_2O$., A.R. B.DH.) in distilled water.

Buffer solutions. They were prepared by mixing requisite volumes of 0.1 M KH_2PO_4 solution and 0.1 M NaOH solution.

Experiment No. 1.—This experiment was carried out to study the influence of different volumes of a 0.01% solution of silver nitrate, on the decomposition of urea by soyabean urease at pH 6.8.

The reaction mixture in each of the flasks I to IX consisted of 60 ml. 4.0% urea solution, 20 ml. buffer solution of pH 6.8, 20 ml. 2.0 soyabean powder extract and 0.2, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0 ml. respectively of 0.01% silver nitrate solution. Flask X contained all the other solutions except silver nitrate and flask XI all the other solutions except silver nitrate and soyabean powder extract. Requisite volumes of distilled water were added to the different flasks to make up the volume of the solution in all the flasks to 140 ml.

The solutions in all the flasks were kept tightly corked and were covered by a few ml. of toluene to prevent bacterial contamination, and this was done in all the experiments. 5 ml. of the reaction mixture from the various flasks were taken out and titrated against N/50 sulphuric acid, daily for five days. Methyl red has been used as the indicator for titrations in all the experiments. The results are given in Table I.

TABLE I

Influence of different volumes (varying from 0.2 ml. to 2.0 ml.) of 0.01% solution of silver nitrate on the decomposition of urea by soyabean urease, at pH 6.8, as indicated by the ml. of N/50 sulphuric acid required to neutralise 5 ml. of the reaction mixture taken out from the different flasks at the following intervals.

Flask	0 Hr. 22°C	24 Hrs. 19°C	48 Hrs. 19°C	72 Hrs. 19°C	96 Hrs. 19°C	120 Hrs. 19°C
I	1·60	10·90	11·30	11·50	11·55	11·60
II	1·25	10·35	11·15	11·20	11·45	11·60
III	0·95	6·90	7·55	7·90	8·10	8·25
IV	0·95	4·40	5·05	5·20	5·30	5·55
V	0·90	1·60	1·80	2·00	2·20	2·35
VI	0·90	1·00	1·05	1·10	1·10	1·15
VII	0·90	0·90	0·95	0·90	0·90	0·95
VIII	0·95	0·90	0·85	0·90	0·90	0·95
IX	0·90	0·90	0·85	0·90	0·90	0·90
X	1·35	13·80	14·95	15·40	15·60	16·00
XI	0·80	0·85	0·90	0·85	0·90	0·85

Experiment No. 2—This experiment was carried out to study the influence of different volumes of 0·01% silver nitrate solution on the decomposition of urea by soyabean urease at pH 7·8.

The reaction mixture in each of the flasks I to X consisted of 60 ml. 4·0% urea soln., 20 ml. 2·0% soyabean powder extract, 20 ml. buffer solution of pH 7·8 and 0·2, 0·4, 0·6, 0·8, 1·0, 1·2, 1·4, 1·6, 1·8 and 2·0 ml. respectively of 0·01% solution of silver nitrate. Flask XI contained all the solutions except silver nitrate and flask XII all the solutions except silver nitrate and soyabean powder extract. Requisite volumes of distilled water were added to different flasks to make up the volume of the solution in all the flasks to 140 ml.

5 ml. of the reaction mixture were taken out from the different flasks, and titrated against N/50 sulphuric acid, daily for five days. The results are given in Table II.

TABLE II

Influence of the different volumes of 0·01% silver nitrate solution, on the decomposition of urea by soyabean urease (at pH 7·8) as observed by the ml. of N/50 sulphuric acid required to neutralise 5 ml. of the reaction mixture taken out from the different flasks at the following intervals.

Flask	0 Hr. 23°C	24 Hrs. 22°C	48 Hrs. 22°C	72 Hrs. 23°C	96 Hrs. 23°C	120 Hrs. 23°C
I	2·10	3·90	4·10	4·45	4·65	4·90
II	2·00	3·80	4·05	4·35	4·40	4·60
III	1·90	3·80	4·05	4·30	4·35	4·55
IV	1·75	3·25	3·40	3·60	3·75	3·90
V	1·70	2·55	2·85	3·30	3·40	3·60
VI	1·70	2·15	2·35	2·60	2·70	2·85
VII	1·70	1·70	1·80	1·90	2·00	2·00
VIII	1·70	1·70	1·80	1·80	1·80	1·80
IX	1·70	1·70	1·75	1·75	1·80	1·80
X	1·70	1·70	1·75	1·75	1·75	1·75
XI	2·35	4·35	4·40	4·70	4·90	5·10
XII	1·60	1·65	1·65	1·60	1·60	1·60

Experiment No. 3—This experiment was carried out to study the influence of different volumes of a 0·01% solution of silver nitrate on the decomposition of urea by soyabean urease at pH 8·8. The contents of the different flasks were the same as in the previous experiment, except that buffer solution of pH 8·8 was used in this experiment.

5 ml. of the reaction mixture from the different flasks were taken out and titrated against N/50 sulphuric acid, daily for five days. The results are given in Table III.

TABLE III

Influence of different volumes of 0·01% silver nitrate solution on the
decomposition of urea by soyabean urease, at pH 8·8, as observed
by the ml. of N/50 sulphuric acid, required to neutralise 5 ml.
of the reaction mixture taken out from the different flasks
at the following intervals.

Flask	0 Hr. 26°C	24 Hrs. 27°C	48 Hrs. 26°C	72 Hrs. 27°C	96 Hrs. 25°C	120 Hrs. 25°C
I	2·55	4·85	5·20	5·25	5·35	5·40
II	2·20	4·85	4·95	5·05	5·10	5·15
III	1·95	3·50	3·80	3·80	4·00	4·00
IV	1·90	2·25	2·30	2·45	2·60	2·65
V	1·85	1·95	2·00	2·00	2·10	2·15
VI	1·85	1·90	1·90	1·90	1·95	1·95
VII	1·85	1·90	1·90	1·90	1·90	1·90
VIII	1·85	1·90	1·90	1·90	1·90	1·90
IX	1·85	1·90	1·90	1·90	1·90	1·90
X	1·85	1·90	1·90	1·90	1·90	1·90
XI	2·85	5·70	5·75	5·85	6·10	6·15
XII	1·85	1·85	1 85	1·80	1·80	1·80

Experiment No. 4—In this experiment, the influence of different volumes of a 0·01% solution of gold chloride on the decomposition of urea by soyabean urease has been studied, at pH 6·8.

The reaction mixture in each of the flasks I to X consisted of 60 ml. 4·0% urea solution, 20 ml. 2·0% soyabean powder extract, 20 ml. buffer solution of pH 6·8, and 0·2, 0·4, 0·6, 0·8, 1·0, 1·2, 1·4, 1·6, 1·8, and 2·0 ml. respectively of 0·01% gold chloride solution. Flask XI contained all other solutions except gold chloride and flask XII all the solutions except gold chloride and soyabean powder extract. Requisite volumes of distilled water were added to different flasks to make up the volume of the solutions in each of the flasks to 140 ml.

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5 ml. of the reaction mixture were taken out from the different flasks and titrated against N/50 sulphuric acid, daily for five days. The results are given in Table IV.

TABLE IV

Influence of the different volumes of a 0·01% solution of gold chloride (at pH 6·8) on the decomposition of urea by soyabean urease, as observed by ml. of N/50 sulphuric acid required to neutralise 5 ml. of the reaction mixture taken out from the different flasks at the following intervals.

Flask	0 hr. 19°C	24 hrs. 18°C	48 hrs. 19°C	72 hrs. 19°C	96 hrs. 19°C	120 hrs. 19°C
I	1·95	9·25	9·75	10·15	10·30	10·35
II	1·80	9·60	9·65	10·00	10·25	10·25
III	1·80	9·50	9·60	9·70	9·70	9·70
IV	1·80	9·30	9·35	9·55	9·60	9·65
V	1·80	8·80	8·80	9·05	9·10	9·05
VI	1·80	8·30	8·25	8·25	8·40	8·35
VII	1·85	8·20	8·10	8·25	8·25	8·25
VIII	2·00	8·20	8·10	8·25	8·25	8·00
IX	1·95	7·50	7·50	7·70	7·90	7·70
X	2·00	7·85	7·80	8·05	8·20	8·00
XI	2·00	9·60	10·70	10·95	11·20	11·20
XII	0·85	0·85	0·90	0·85	0·85	0·85

Experiment No. 5—This experiment was carried out to study the influence of different volumes of 0·01% solution of gold chloride on the decomposition of urea by soyabean urease at pH 7·8. The contents of the different flasks were the same as in the previous experiment except that buffer solution of pH 7·8 was used in this experiment.

5 ml. of the reaction mixture were taken out from the different flasks, and titrated against N/50 sulphuric acid, daily for five days. The results are given in Table V.

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TABLE V

Influence of different volumes of 0·01% gold chloride solution, on the decomposition of urea by soyabean urease, at pH 7·8, as observed by ml. of N/50 sulphuric acid required to neutralise 5 ml. of reaction mixture taken out from the different flasks at the following intervals.

Flask	0 Hr. 17°C	24 hrs. 17°C	48 hrs. 17°C	72 hrs. 18°C	96 hrs. 19°C	120 hrs. 19°C
I	1·95	2·75	2·80	2·90	3·10	3·10
II	1·90	2·75	2·80	2·85	3·00	3·00
III	1·95	2·80	2·80	2·85	3·00	3·00
IV	1·95	2·75	2·75	2·85	3·00	3·00
V	1·95	2·75	2·80	2·85	3·00	3·00
VI	1·95	2·75	2·80	2·90	3·00	3·00
VII	1·90	2·80	2·80	2·85	3·00	3·00
VIII	1·95	2·75	2·80	2·85	2·95	3·00
IX	1·95	2·75	2·75	2·85	2·90	2·90
X	1·95	2·70	2·75	2·85	2·90	2·90
XI	2·00	2·75	2·90	3·00	3·10	3·15
XII	1·55	1·55	1·55	1·55	1·55	1·55

Experiment No. 6—This experiment was carried out to study the influence of different volumes of a 0·01% gold chloride solution on the decomposition of urea by soyabean urease at pH 8·8. The contents of the different flasks were the same as in the previous experiment except that buffer solution of pH 8·8 was used in this experiment.

5 ml. of the reaction mixture were taken out and titrated against N/50 sulphuric acid, daily for five days. The results are given in Table VI.

TABLE VI

Influence of different volumes of 0·01% gold chloride solution on the decomposition of urea by soyabean urease, at pH 8·8, as observed by the ml. of N/50 sulphuric acid required to neutralise 5 ml. of the reaction mixture taken out from the different flasks at the following intervals.

Flask	0 Hr. 18°C	24 hrs. 17°C	48 hrs. 16°C	72 hrs. 16°C	96 hrs. 15°C	120 hrs. 17°C
I	2·25	3·90	4·20	4·30	4·30	4·35
II	2·20	3·80	2·95	4·20	4·20	4·20
III	2·25	3·80	4·05	4·25	4·25	4·25
IV	2·25	3·80	4·00	4·15	4·25	4·25
V	2·25	3·80	4·00	4·15	4·25	4·25
VI	2·20	3·75	3·95	4·10	4·15	4·15
VII	2·25	3·75	3·95	4·10	4·15	4·15
VIII	2·25	3·65	3·75	3·85	3·85	4·00
IX	2·25	3·65	3·75	3·85	3·85	4·00
X	2·25	3·65	3·80	3·85	3·85	4·00
XI	2·50	4·05	4·35	4·35	4·50	4·50
XII	1·80	1·85	1·85	1·80	1·80	1·80

Experiment No. 7—In this experiment, the influence of different volumes of a 0·01% solution of copper sulphate, on the decomposition of urea by soyabean urease at pH 6·8 has been studied. The reaction mixture in each of the different flasks I to X consisted of 60 ml. 4·0% urea solution, 20 ml. buffer solution of pH 6·8, 20 ml. 2·0% soyabean powder extract and 0·2, 0·4, 0·6, 0·8, 1·0, 1·2 1·4, 1·6, 1·8 and 2·0 ml. respectively of 0·01% copper sulphate solution. Flask XI contained all other solutions except copper sulphate solution and flask XII all the solutions except copper sulphate and soyabean powder extract. Requisite volumes of distilled water were added to different flasks to make up the volume of the solutions in all the flasks to 140 ml.

5 ml. of the reaction mixture were taken out from the various flasks and titrated against N/50 sulphuric acid, daily for five days. The results are given in Table VII.

TABLE VII

Influence of the different volumes of 0·01% solution of copper sulphate
on the decomposition of urea by soyabean urease at pH 6·8, as
observed by the ml. of N/50 sulphuric acid required to neutralise
5 ml. of the reaction mixture taken out from the different
flasks at the following intervals.

Flask	0 Hr. 19°C	24 hrs. 18°C	48 hrs. 17°C	72 hrs. 17°C	96 hrs. 17°C	120 Hrs. 20°C
I	1·80	14·80	16·95	18·10	18·10	18·15
II	1·75	12·80	13·70	14·50	14·55	14·55
III	1·75	11·20	11·90	12·30	12·30	12·25
IV	1·75	9·70	10·40	10·75	10·75	10·80
V	1·85	8·50	9·10	9·30	9·30	9·30
VI	1·80	7·60	7·90	7·95	8·05	8·00
VII	1·80	6·30	6·60	6·65	6·85	6·85
VIII	1·80	6·10	6·20	6 35	6·40	6·40
IX	1·80	5·50	5·75	5·90	6·00	6·00
X	1·75	5·30	5·30	5·50	5·60	5·60
XI	2·15	19·00	23·00	24·70	25·70	26·00
XII	0·85	0·85	0·85	0·90	0·90	0·90

Experiment No. 8—This experiment was carried out to study the influence of
different volumes of a 0·01% solution of copper sulphate on the decomposition of
urea by soyabean urease at pH 7·8. The contents of the different flasks were the
same as in the previous experiment except that buffer solution of pH 7·8 was used
in this experiment.

5 ml. of the reaction mixture from the different flasks were taken out and
titrated against N/50 sulphuric acid daily for five days. The results are given in
Table VIII.

TABLE VIII

Influence of different volumes of a 0·01% solution of copper sulphate on the decomposition of urea by soyabean urease, at pH 7·8, as observed by ml. of N/50 sulphuric acid required to neutralise 5 ml. of the reaction mixture taken out from the different flasks at the following intervals.

Flask	0 hr. 27°C	24. hrs. 26°C	48 hrs. 27°C	72 hrs. 25°C	96 hrs. 25°C	120 hrs 25°C
I	2·10	3·60	3·90	4·00	4·15	4·30
II	2·10	3·40	3·60	3·75	3·95	4·10
III	2·10	3·30	3·60	3·65	3·90	3·95
IV	2·10	3·10	3·20	3·30	3·50	3·65
V	2·10	2·90	3·10	3·15	3·40	3·55
VI	2·05	2·90	2·90	3·00	3·30	3·30
VII	2·05	2·60	2·80	2·95	3·30	3·30
VIII	2·05	2·60	2·80	2·95	3·10	3·20
IX	2·05	2·60	2·75	2·95	3·10	3·20
X	2·05	2·50	2·75	2·90	3·10	3·20
XI	2·15	5·20	5·75	5·80	6·00	6·10
XII	1·60	1·60	1·60	1·60	1·60	1·60

Experiment No. 9—This experiment was carried out to study the influence of different volumes of 0·01% solution of copper sulphate on the decomposition of urea by soyabean urease at pH 8·8. The contents of the different flasks were the same as in the previous experiment, except that buffer solution of pH 8·8 was used in this experiment.

5 ml. of the reaction mixture from the different flasks were taken out and titrated against N/50 sulphuric acid daily for five days. The results are given in Table IX.

TABLE IX

Influence of different volumes of 0·01% solution of copper sulphate on
the decomposition of urea by soyabean urease, at pH 8·8, as
observed by the ml. of N/50 sulphuric acid required to neutralise
5 ml. of the reaction mixture taken out from the various
flasks at the following intervals.

Flask	0 Hr. 27°C	24 hrs. 25°C	48 hrs. 25°C	72 hrs. 25°C	96 hrs. 25°C	120 hrs. 25°C
I	2·40	3·70	3·85	3·90	4·05	4·05
II	2·30	3·35	3·45	3·55	3·65	3·70
III	2·30	3·20	3·30	3·35	3·45	3·50
IV	2·30	2·95	3·00	3·10	3·15	3·30
V	2·25	2·75	2·75	2·80	2 90	3·00
VI	2·25	2·65	2·65	2·75	2·80	2·90
VII	2·20	2·55	2·60	2·65	2·70	2·80
VIII	2·20	2·50	2·50	2·50	2·55	2·65
IX	2·10	2·40	2·50	2·50	2·55	2·60
X	2·10	2·40	2·50	2·50	2·50	2·60
XI	2·45	3·85	3·90	3·90	4·05	4·10
XII	1·80	1·80	1·80	1·80	1·80	1·80

DISCUSSION

These experiments were performed with a view to investigate the comparative
influnce of Ag^+, Au^{+++}, and Cu^{++} ions on the decomposition of urea by soyabean
urease. The influence of different volumes of 0·4139% and 0·1% solutions of
silver nitrate, on the decomposition of urea by soyabean urease at pH 6·8, was first
studied but, it was found that there occurred either no decomposition or very little
decomposition of urea even after five days. A more dilute solution (0·01%) was
therefore, tried. Experiment No. 1 was carried out to study the influence of
different volumes (varying from 0·2 ml. to 2·0 ml.) of 0·01% solution of silver
nitrate on the decomposition of urea by 20 ml. of 2% soyabean powder extract at
pH 6·8. The results of the experiment show that the inhibition of the enzymic
activity of urease, increases with an increase in the volume of silver nitrate solution
from 0·2 ml. to 2·0 ml. With 0·2 ml. of silver nitrate solution, the inhibition is very
little, but with 2·0 ml. of it, the reaction almost stops totally.

Experiment No. two and three were carried out to study the influence of
different volumes of 0·01% solution of silver nitrate on the decomposition of urea by
soyabean urease at pH 7·8 and 8·8 respectively. These experiments were carried
out to study the influence of pH on the inhibitory effect of Ag^+ ions. The results of
these experiments indicate that Ag^+ ions act as strong inhibitors for urease at pH

6·8, 7·8 and 8·8 and there is very little difference in the inhibition at the different pH studied.

In order to study the influence of gold ions, different volumes of a 0·1% solution of gold chloride were first tried, but it was found that there was very little decomposition of urea. So in this case also a 0·01% solution of gold chloride was tried, at pH 6·8, in experiment number four. The volume of this solution was varied from 0·2 ml. to 2·0 ml. The results indicate that Au^{+++} ions act as inhibitors and the inhibition increases with an increase in the concentration of Au^{+++} ions. Experiment number five and six were carried out to study the influence of different volumes of 0·01% solution of gold chloride on the decomposition of urea by soyabean urease at pH 7·8 and 8·8 respectively. These experiments were carried out to study the influence of pH on the inhibitory effect of Au^{+++} ions on the decomposition of urea by soyabean urease. The results of these experiments indicate that the inhibition is maximum at pH 6·8. There is very little inhibition at pH 7·8 and 8·8.

The influence of copper ions was first studied, by using different volumes of 0·3041% and 0·1% solutions of copper sulphate, but there occurred either no decomposition or very little decomposition of urea. A 0·01% solution of copper sulphate was, therefore, tried at pH 6·8, in experiment no. 7. The results of this experiment indicate that Cu^{++} ions act as strong inhibitors, and the inhibition increases with an increase in the concentration of Cu^{++} ions. Experiment numbers eight and nine were carried out to study the influence of different volumes of 0·01% copper sulphate solution on the decomposition of urea by soyabean urease at pH 7·8 and 8·8 respectively. These experiments indicate that inhibition by copper ions is much more at pH 6·8 than at pH 7·8 and 8·8.

The experiments with Ag^+, Au^{+++}, and Cu^{++} ions indicate that silver ions have the greatest inhibitory influence and the gold ions the least. The inhibitory influence of Cu^{++} ions is greater than that of Au^{+++} ions, but is much less than that of Ag^+ ions.

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INFLUENCE OF THE SOURCE OF CARBON ON PHOTOCHEMICAL FIXATION OF NITROGEN IN AQUEOUS MIXTURES CONTAINING MOLYBDIC ACID AS THE CATALYST

By

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ABSTRACT

Photochemical fixation of nitrogen is three folds increased when paraformaldehyde of the mixture of paraformaldehyde, water and molybdic acid is substituted by tartaric acid. In this mixture of 50 ml volume 0·6134 mg of molecular nitrogen is fixed on an exposure of about 450 hours as compared to only 0·2597 mg. of nitrogen fixation in similar mixture containing paraformaldehyde as the source of carbon on similar exposure.

The quantitative aspect of the photochemical fixation of nitrogen observed by Bahadur, Ranganayaki, and Santamaria[1] in 1948 is being studied and the role of different catalysts on this fixation is under publication elsewhere. The influence of change of carbon source has been examined statistically and it has been observed that the fixation is greatly influenced by the nature of the carbon compound present in the mixture.

Originally Bahadur *et. al.* employed paraformaldehyde as the source of carbon and colloidal molybdenum oxide as the catalyst. In the experiment described in the present communication; molybdic acid has been used as catalyst and the fixation of nitrogen in the mixture containing paraformaldehyde has been compared with that in an mixture containing tartaric acid as the source of carbon.

EXPERIMENTAL

Nine mixtures containing 0·3000 gm of analytically pure tartaric acid, 0·0500 gm of pure molybdic acid and 50 ml of glass distilled water were prepared in 150 ml Sigcol conical flasks. All these flasks were plugged with surgical cotton and

the mixtures were sterilised at 15 lbs steam pressure for about 30 minutes. After cooling, the mouths of the flasks were sealed with polythene paper and transparent adhesive tape to prevent the loss of water by evaporation and avoid contact with outside air. This eliminated contact of the mixture with any traces of ammonia or amine which may be present in the atmospheric air. Another similar set of nine mixtures was prepared using the same amount of paraformaldehyde instead of tartaric acid.

Four of the flasks of each set were exposed to sunlight and another four were kept covered with four fold thick black cotton cloth. One flask was kept for the estimation of nitrogen and for the identification of amino acids. The period of exposure was the time for which the flasks were kept in sunlight. The variation of temperature during the exposure was noted from time to time.

Nitrogen present in the control mixture and in the mixtures exposed to sunlight for about 450 hours was estimated in a semi-micro Kjeldahl's apparatus using A. R. chemicals. The identication of amino acids was carried out using circular paper chromatography technique[2]. The two running solvents used for the seperation of amino acids were:

(1) *n*-Butanol-water-glacial acetic acid (4 : 5 : 1).

(2) Phenol-water (80 : 20) in an atmospher of ammonia.

The results obtained by the analysis of the above mixtures are tabulated.

DISCUSSION

Tartaric acid fixes much more nitrogen as compared to paraformaldehyde in the mixture under experimental conditions described in the present communication. The statistical study of this fixation shows that the fixation of nitrogen in both the mixtures i. e. one which contains paraformaldehyde and the one which contains tartaric acid as the source of carbon, is quite significant. For the same period of exposure the quantity of nitrogen fixed in 50 ml of the mixture was 0·2597 mg. with paraformaldehyde and 0·6134 mg. with tartaric acid as carbon source.

The statistical data of this fixation is described below:

Photochemical fixation of nitrogen in mixtures containing tartaric acid as the source of carbon and molybdic acid as the catalyst after an exposure of about 450 hours.
(Variation of temperature during the exposure : 32°C to 52°C)

Serial number	Condition	Titre reading of N/48·5 sulphuric acid in ml. for ammonia produced by the mixture	Statistical average	Nitrogen fixed in mg. in the mixture	Rf. values of amino acids in Butanol-water-acetic acid	Rf. values of amino acid in Phenol-water ammonia	Amino acids identified	Mg. of nitrogen fixed by light in the total mixture
1	L	16·1						
2	I	16·2	15·975 ±0·1601	4·611 ±0·0462	Rf 0·47	Rf 0·74	Proline	0·297
3	G	15·5			Rf 0·40	Rf 0·51	Alanine	
4	H	16·1				Rf 0·37	Serine	
	T					Rf 0·20	Glutamic acid	
5	D	14·8			Rf 0·48	Rf 0·78	Proline	
6	A	15·1	15·075 ±·1213	4·351 ±0·0350	Rf 0·40	Rf 0·37	Serine	
7	R	15·4				Rf 0·19	Glutamic acid	
8	K	15·0						
9	Control	15·0	—	4·329	Nil	Nil	Nil	

Statistical significance factor 3 $(a^2 + b^2)^{1/2}$ < the diff. of the two average titre readings, where a and b are the statistical errors of the two averages. Since 0·6024 <0·9060, therefore the result is significant.

Remark:—Four amino acids were synthesised in the mixtures exposed to light whereas similar mixture kept in dark indicated the formation of only three amino acids. The amino acid rings developed on the chromatogram with the mixtures exposed to light were much intense in colour than in similar mixtures kept in dark indicating thereby greater concentration of amino acids synthesised in the mixtures exposed to light. The intensity of the rings of individual amino acids synthesised in the mixtures was of the following order :

Light : Glutamic acid> serine > proline> alanine
Dark : Glutamic acid> serine > proline.

Photochemical fixation of nitrogen in the mixture containing paraformaldehde as the source of carbon and molybdic acid as the catalyst after an exposure of about 450 hours

(Variation of temperature during the exposure : 32°C to 52°C)

Serial number	Condition	Titre reading of N/48·5 sulphuric acid in ml. for amonia produced by the mixture	Statistical average	Nitrogen fixed in mg. in the mixture	Rf. values of amino-acids in Butanol-water acetic-acid	Rf. values of amino-acids in Pheonal-water ammonia	Amino acid indentified	Mg. of Nitrogen fixed by light in the total mixture
1	L, I	21·5						
2	G	21·0	21·125 ±0·1250	6·098 ±0·0312	Rf 0·54	Rf 0·78	Proline	
3	H	21·0			Rf 0·34	Rf 0·51	Alanine	
4	T	21·0				Rf 0·33	Serine	
						Rf 0·21	Glutamic-acid	
5	D	19·0	19·000 ±0·000	5·484 ±0·0000	Rf 0·54	Rf 0·79	Proline	0·6134
6	A	19·0			Rf 0·36	Rf 0·50	Alanine	
7	R	19·0				Rf 0·34	Serine	
8	K	19·0				Rf 0·19	Glutamic-acid	
9	Control	18·5	—	5·340	Nil	Nil	Nil	Nil

Statistical significance factor $3\ (a^2 + b^2)^{1/2} <$ the difference of the two average reading, where a and b are the statistical errors of the two averages. Since $0·375 < 2·125$. Therefore the result is significant.

Remarks :—Though the nature of the amino acids synthesised in the mixtures exposed to light was similar to the amino-acids formed in the mixtures kept in dark, the intensity and breadth of the amino acid rings developed on the chromatogram in the case of the mixtures exposed to light were far more prominent than in the similar mixture kept in dark. The intensity of the individual amino acid rings was of the following order.

Glutamic acid> Serine> Proline> Alanine.

Source of carbon	Condition	Average ml of N/48·5 sulpuric acid to titrate liberated ammonia	Statistical Error	Significance factor	Diff. of two averages	Remarks
Parafor-maldehyde.	Light	15·975	± 0·1601			
	Dark	15·075	± 0·1213	0·6012	0·9000	Result is significant
Tartaric acid.	Light	21·125	± 0·1250			
	Dark	19·000	± 0·0000	0·3750	2·1250	Result is significant

Thus it is proved that tartaric acid is a better source of carbon than paraformaldehyde in the photochemical fixation of nitrogen in aqueous mixtures containing molybdic acid as the catalyst.

ACKNOWLEDGMENT

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STUDY OF STABILITY OF SOME METAL-ORGANO SOLS — PART I

By

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ABSTRACT

The experimental data for the stability of some gel forming metal-organo sols are presented. The variation of stability and rates of gelation with coagulant concentration is discussed. The rate of gelation decreases with the square root of coagulant concentration according to the Packter's equation $\log W = C_1 \gamma^4 - C_2 \gamma^2 \sqrt{C_e}$. Addition of electrolyte leads to slow coagulation of the anisometric particles and ordered orientation giving rise to gel structure. Further addition of electrolyte corresponds to rapid gelation and syneresis.

It is well known that very often addition of electrolytes to concentrated sols of anisometric particles leads to gelation. According to Verwey and Overbeek (1) the stability factor W for a sol is correlated with the energy of interaction V between the colloidal particles, according to the equation :

$$W = 2 \int_{2}^{\infty} e^{V/KT} \cdot \frac{ds}{s^2}$$

Where $s = r/a$, r being the distance between the colloidal particles and a being the radius. Large amount of available experimental data satisfactorily explains the above relation and shows that gelation is a slow coagulation process. In several publications (2) from these laboratories it has been shown that gelation corresponds to slow coagulation followed by a stable structure formation, despite that certain repulsion exists between adjacent particles. The formation of structurations in these gel forming systems have been studied in detail using electron microscopy, streaming birefringence and light scattering methods.

Recently Packter (3) has suggested that coagulation of dilute sols with such particles occurs by a perpendicular orientation of adjacent particles. Packter in one of his recent publications has calculated zeta-potentials for certain sols. He has given the following relation for the coagulation of dialysed plate and rod (needle) like sols followed by perpendicular orientation at 20°C by monovalent ions :

$$\frac{d \log_{10} W}{d \sqrt{C_e}} = 300 \gamma^2$$

where $- \log W = \log t/\bar{t}$ ($\bar{t}$ is the limiting time for coagulation) and C_e is the concentration of the electrolyte.

The value of surface potential (ψ_δ) has been calculated by the following relation (Cf. 3) :

$$\gamma = \frac{\exp. (.z/2 - 1)}{\exp. (.z/2 + 1)}$$

where $z = V e \psi_\delta / KT$, V is the valency of the coagulating ions, T is the sol temperature, e and K are the physical constants.

[88]

Packter has plotted log W as a function of $\sqrt{C_e}$ in several sols such as metal hydroxide sols, vanadic acid and tungstic acid sols from the available data and has established a linear relation between log W and $\sqrt{C_e}$ given by the expression :

$$\log W = C_1 \gamma^4 - C_2 \gamma^2 \sqrt{C_e}$$

where C_1 and C_2 are constants

In this paper we are presenting our results on the variation of the stability of some unstirred gel yielding metal adipate sols as a function of the gelating electrolyte concentration employing the Packter's equation.

<div align="center">EXPERIMENTAL</div>

Iron Adipate Sols :

Three samples of iron adipate sols were prepared by adding to a fixed quantity of the ferric chloride solution, different amounts of sodium adipate solution of suitable concentrations so as to obtain a clear stable sol. The iron content in all the three samples was kept constant by estimating it and diluting the sols with distilled water wherever necessary. The total volume of 500 ml. was kept the same in all samples. The three sols (A_1), (B_1) and (C_1) had the following compositions :

Volume of 0·1666 M Ferric chloride in each sample = 200·0 ml.

Volume of 0·1666 M Sodium adipate :

in sol (A_1) = 50·0 ml.

in sol (B_1) = 60·0 ml.

in sol (C_1) = 70·0 ml.

The sols were purified by dialysis for a period of 48 hours at room temperature. The sols were preserved in Jena glass bottles at low temperature to avoid the effect of ageing.

Zirconium Adipate Sols :

Three samples of the zirconium adipate sols were prepared by mixing a fixed quantity of zirconium nitrate and different amounts of sodium adipate, keeping the total volume of 500 ml. same in all cases. The sols were purified by dialysis and preserved in Jena glass bottles at low temperatures. By estimating the zirconium content in each case, the amount of the same was kept constant by dilution of the sol with distilled water.

Sols (A_2), (B_2) and (C_2) had the following compositions. Volume of 0·0833 M zirconium nitrate in each sample = 250 ml.

Volume of 0·0417 M sodium adipate :

in sol (A_2) = 160 ml.

in sol (B_2) = 180 ml.

in sol (C_2) = 200 ml.

The sols were dialysed for 72 hours.

<div align="center">[89]</div>

Procedure :

For the observations of the gelling time, a fixed amount of the sol was taken in a series of test tubes. In another set of test tubes, were taken different volumes of the standard solution of the gelating electrolyte KCl or K_2SO_4, diluted with the requisite amount of distilled water to make the total volume same in all cases. The test tubes were thermostatised at $32 \pm 0.1°C$ for half an hour. The sol and the electrolyte were mixed together by mixing back and forth twice and the gelling time was recorded according to Bose and Mushran (4). The stability W of the gelling sols was determined from the relation: $\log W = \log t/t$ where $\bar{t}$ is the limiting time for rapid gelation. The results are presented in the following tables :

TABLE I

Stability (W) depending upon the varying amounts of the electrolyte

Volume of the sol A_1　　　　$=$　3.00 ml.

Total volume　　　　　$=$　4.00 ml.

Limiting time for rapid gelation $\bar{t} =$　8.50 mins.

KCl in $\left(\dfrac{\text{gm. eq. per litre}}{100\sqrt{C_e}}\right)^{1/2}$	Gelling time t in mins.	$\log W = t/\bar{t}$
4.98	8.5	0.0000
4.72	14.5	0.2320
4.46	22.0	0.4130
4.17	35.5	0.6208
3.86	54.5	0.8070
3.52	86.0	1.0051

TABLE II

Stability (W) depending upon the varying amounts of the electrolyte

Volume of the sol B_1　　　$=$　3.00 ml.

Total volume　　　　$=$　4.00 ml.

Limiting time for rapid gelation $\bar{t} =$　5.50 mins.

KCl in $\left(\dfrac{\text{gm. eq. per litre}}{100\sqrt{C_e}}\right)^{1/2}$	Gelling time t in mins.	$\log W = t/\bar{t}$
4.98	5.5	0.0000
4.72	9.0	0.2138
4.46	13.5	0.3899
4.17	22.0	0.6020
3.86	35.0	0.8037
3.52	56.0	1.0078

Stability (W) depending upon the varying amounts of the electrolyte

Volume of the sol C_1 =   3·00 ml.

Total volume   =   4·00 ml.

Limiting time for rapid gelation $\bar{t}$ =   4·00 mins.

KCl in $\dfrac{(\text{gm. eq. per litre})^{1/2}}{100 \sqrt{C_e}}$	Gelling time t in mins.	$\text{Log } W = t/\bar{t}$
4·98	4·0	0·0000
4·72	6·0	0·1761
4·46	10·0	0·3979
4·17	16·0	0·6021
3·86	24·0	0·7782
3·52	28·0	0·9777

TABLE IV

Stability (W) depending upon the varying amounts of the electrolyte

Volume of the sol A_1 =   3·00 ml.

Total volume   =   4·00 ml.

Limiting time for rapid gelation $\bar{t}$ =   6·00 mins.

K_2SO_4 in $\dfrac{(\text{gm. eq. per litre})^{1/2}}{100 \sqrt{C_e}}$	Gelling time t in mins.	$\text{Log } W = t/\bar{t}$
2·41	6·0	0·0000
2·28	11·5	0·2825
2·15	23·0	0·5835
2·02	47·0	0·8939
1·87	90·0	1·1760

TABLE V -

Stability (*W*) depending upon the varying amounts of the electrolyte

Volume of the sol B_1 = 3·00 ml.

Total volume = 4·00 ml.

Limiting time for rapid gelation $\bar{t}$ = 4·50 mins.

K_2SO_4 in $\dfrac{\text{(gm. eq. per litre)}^{1/2}}{100 \sqrt{C_e}}$	Gelling time t in mins.	Log $W = t/\bar{t}$
2·41	4·5	0·0000
2·28	8·0	0·2499
2·15	16·5	0·5643
2·02	33·0	0·8653
1·87	65·0	1·1597

TABLE VI

Stability (*W*) depending upon the varying amounts of the electrolyte

Volume of the sol C_1 = 3·00 ml.

Total volume = 4·00 ml.

Limiting time for rapid gelation $\bar{t}$ = 3·50 mins.

K_2SO_4 in $\dfrac{\text{(gm. eq. per litre)}^{1/2}}{100 \sqrt{C_e}}$	Gelling time t in mins.	Log $W = t/\bar{t}$
2·41	3·5	0·0000
2·28	6·0	0·2341
2·15	11·0	0·4973
2·02	22·0	0·7983
1·87	38·0	1·0357

The results presented in tables I to VI are shown graphically in figures 1 and 2.

Fig. 1.—log W versus $\sqrt{_jC_e}$

Fig. 2.—log W versus $\sqrt{C_e}$

[94]
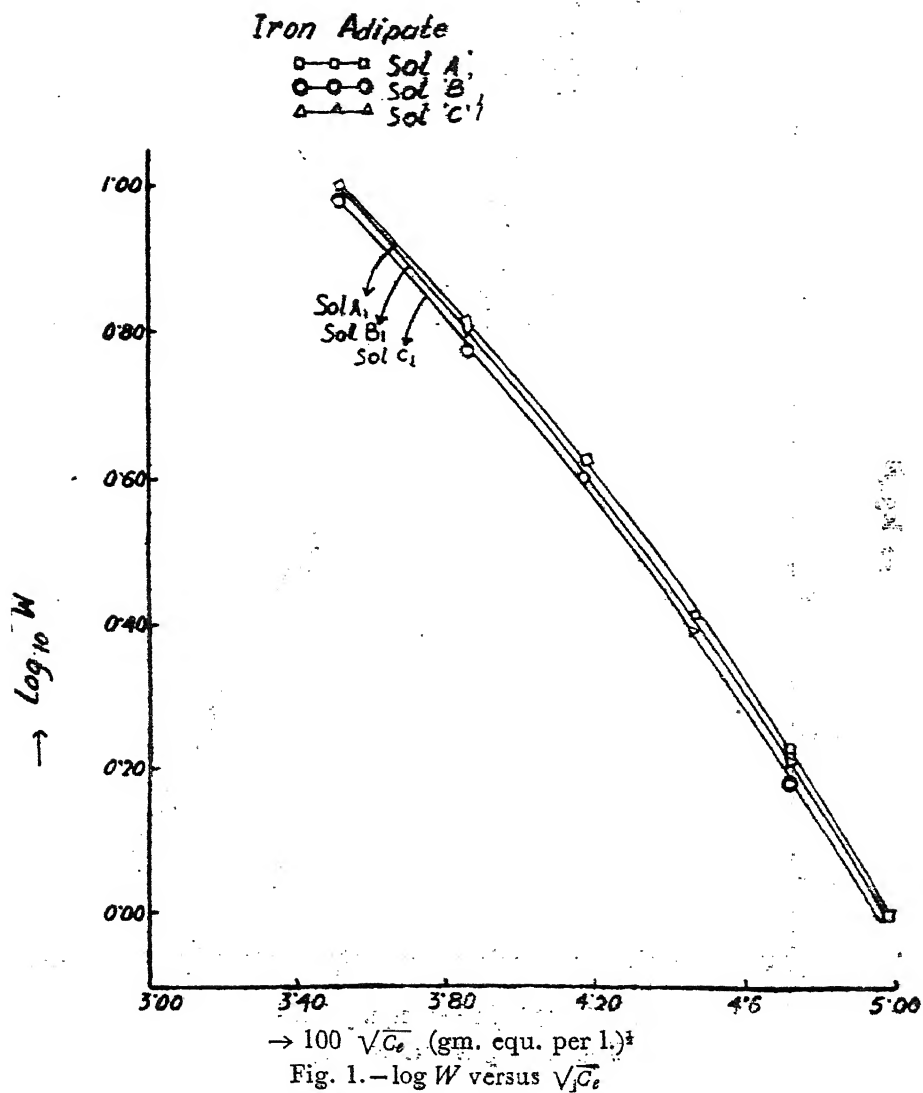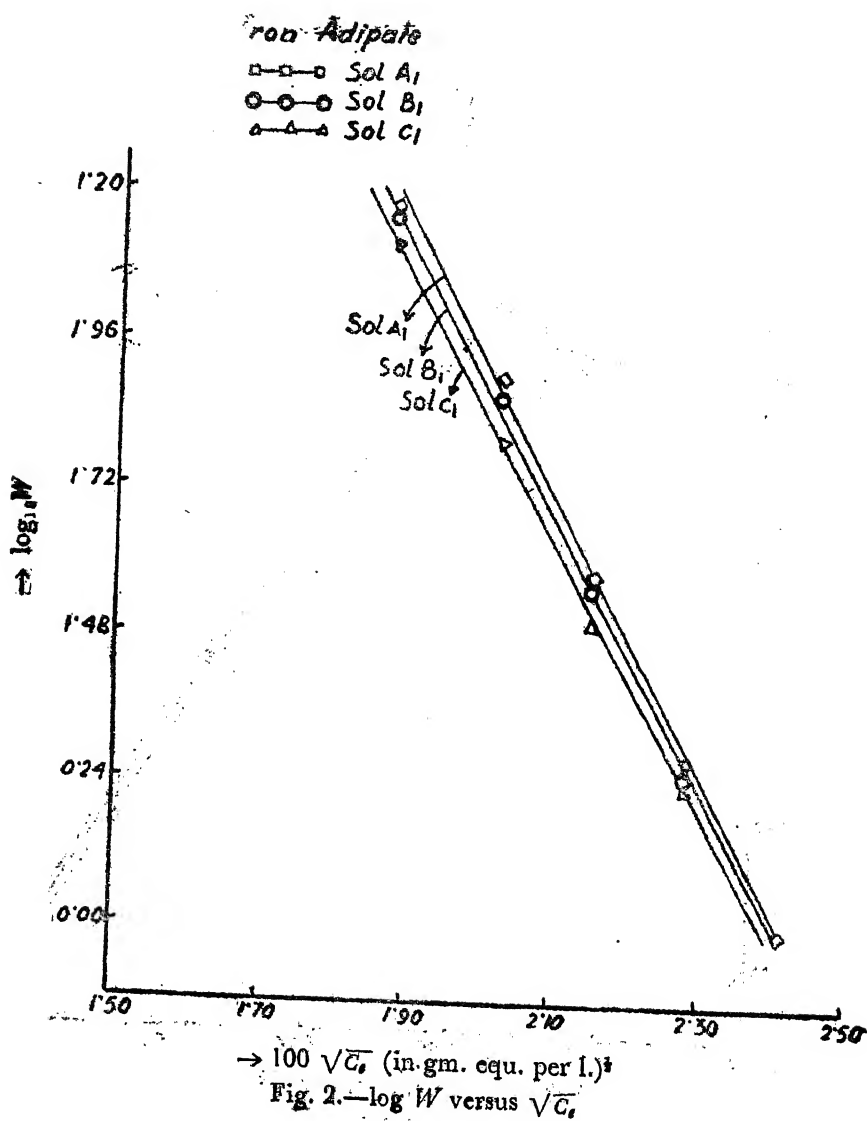
TABLE VII

Stability (W) depending upon the varying amounts of the electrolyte

Volume of the sol A_2	=	4·00 ml.
Total volume	=	5·00 ml.
Limiting time for rapid gelation $\bar{t}$	=	3·00 mins.

KCl in $\dfrac{(\text{gm. eq. per litre})^{1/2}}{100 \sqrt{C_e}}$	Gelling time t in mins.	Log $W = t/\bar{t}$
11·14	3·0	0·0000
10·58	7·5	0·3980
9·95	16·0	0·7270
9·33	35·0	1·0670
9·00	50·0	1·2219
8·66	74·0	1·3921
8·25	110·0	1·5643
7·87	160·0	1·7270

TABLE VIII

Stability (W) depending upon the varying amounts of the electrolyte

Volume of the sol B_2	=	4·00 ml.
Total volume	=	5·00 ml.
Limiting time for rapid gelation $\bar{t}$	=	2·00 mins.

KCl in $\dfrac{(\text{gm. eq. per litre})^{1/2}}{100 \sqrt{C_e}}$	Gelling time t in mins.	Log $W = t/\bar{t}$
11·14	2·0	0·0000
10·58	4·0	0·3010
9·95	9·0	0·6532
9·33	19·0	0·9178
9·00	29·0	1·1614
8·66	42·0	1·3222
8·25	59·0	1·4699
7·87	88·0	1·6435

TABLE IX

Stability (W) depending upon the varying amounts of the electrolyte

Volume of the sol C_2 = 4·00 ml.
Total volume = 5·00 ml.
Limiting time for rapid gelation $\bar{t}$ = 1·50 mins.

KCl in (gm. eq. per litre) 1/2 $100 \sqrt{C_e}$	Gelling time t in mins.	Log $W = t/\bar{t}$
10·58	1·5	0·0000
9·95	2·5	0·2218
9·33	5·5	0·5643
8·66	12·0	0·9031
7·87	26·0	1·2389
7·07	57·0	1·5798
6·67	80·0	1·7270
6·08	120·0	1·9031

The results presented in tables VII to IX are shown graphically in Fig. 3.
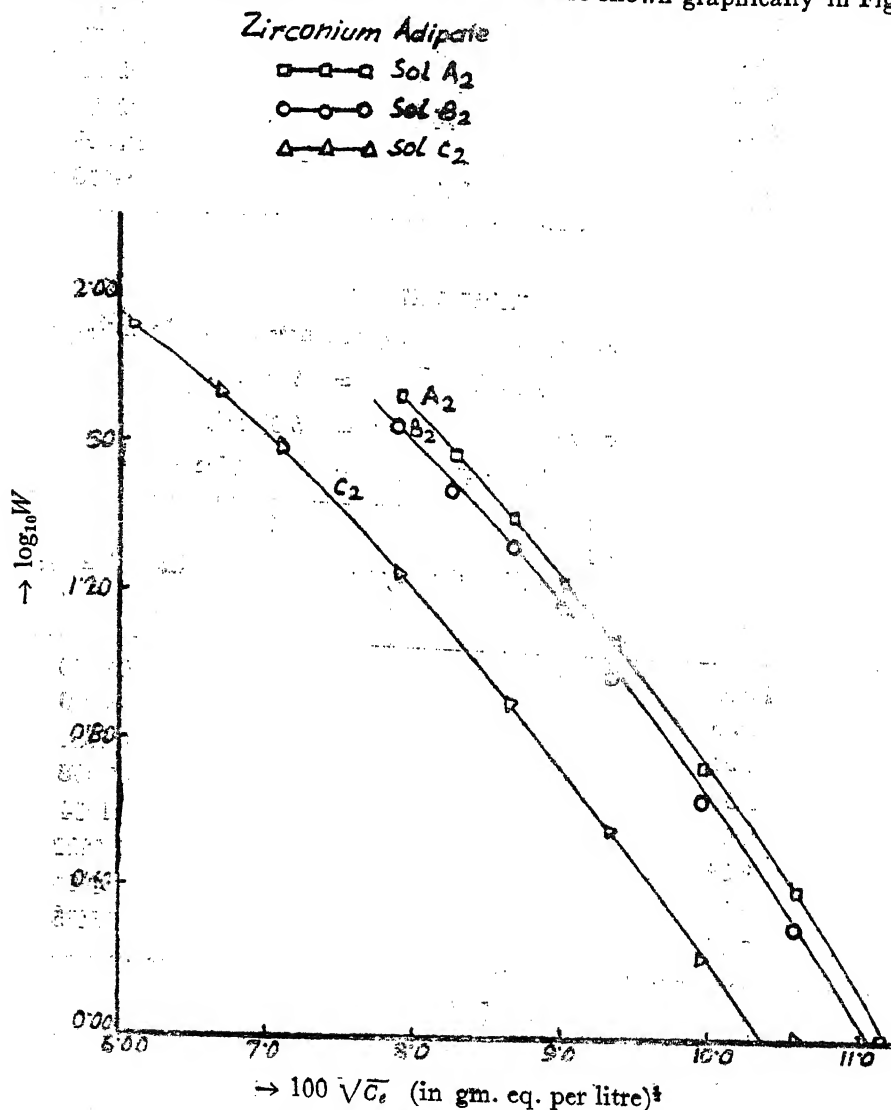
Fig. 3.—log W versus $\sqrt{C_e}$

DISCUSSION

It is well known that the mechanism operative during the coagulation of sols by inorganic electrolytes is the compression of the double layer leading to a reduction of the repulsive potential and a decrease of the stability. A perusal of the data presented in Tables I to IX show that the stability of the metal adipate sols investigated in this paper decrease on addition of electrolytes. The stabilities have been determined from the relation $\log W = \log t/\bar{t}$, where $\bar{t}$ is the limiting time of rapid gelation when the repulsion energy between adjacent colloid particles falls to very low values. An inspection of Figs. 1 to 3 shows a linear relation between $\log W$ and $\sqrt{C_s}$ suggesting that slow thixotropic gelation is a slow coagulation process, involving oriented aggregation of the colloidal units.

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ADIABATIC GRADIENT IN STELLAR ATMOSPHERES

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ABSTRACT

There are two methods of calculating the adiabatic gradient required for a convective zone. One is from entropy considerations and the other from energy considerations. Many authors have tried the former method. In this paper an expression for the adiabatic gradient for a mixture of elements including the effect of radiation field is derived from energy considerations. The value obtained from this method is found to be in good agreement with that obtained from entropy considerations.

INTRODUCTION

From the stellar observations, especailly the limbdarkening data of the sun, it is found that the outermost layers of a star are in radiative equilibrium. But from theoretical considerations it is obvious that the atmosphere, when extended to greater optical depth cannot be in stable radiative equilibrium. The convective layer below the photosphere is present in almost all the stars except few very hot ones. The main reason for setting up of this convection is the ionisation of some material. During the ionisation lot of energy is diverted towards this ionisation, creating larger temperature gradient. In the very hot stars the ionisation is almost complete and hence no convection. Schwarzschild (1906) was the first to study the mechanical stability of stellar atmosphere under radiative equilibrium. He showed that the atmosphere will be convectively ustable if the radiative temperature gradient at any level in a stellar atmosphere exceeds the adiabatic temperature gradient corresponding to the same values of temperature and pressure. In the outer convective zone of a star the transport of energy by convection is quite appreciable. Due to the convective motion, the ratiative temperature gradient will be reduced. The actual temperature gradient present in the convective zone will be greater than the adiabatic temperature gradient but less than radiative temperature gradient (Woolley and Stibbs, 1953). The exact value of the actual temperature gradient present depends on the relative importance of the convictive and radiative transports of energy. But for all practical purposes one usually uses the adiabatic temperature gradient which is the lower limit of the temperture gradient expected in the convective zone. Hence the knowledge of the adiabatic gradient appropriate to the physical conditions existing in the convective zone is essential before any study of the physical parameters in the zone can be made.

The adiabatic gradient for a gas is given by the expression,

$$\left(\frac{d \log T}{d \log P_g} \right)_{ad} = \frac{\Gamma - 1}{\Gamma} \qquad (1)$$

In this expression quantity Γ is a function of ionisation being $5/3$ for monoatomic gas. Hence as the ionisation varies, this Γ also varies and we cannot have any simple relation for this Γ valid for the whole range of convective zone. Therefore

one is forced to calculate the ionisation and consequently adiabatic gradient for every point in the model atmosphere. The effect of the ionisation on the variation of Γ was shown by Fowler and Guggenheim, (1925). Unsöld (1930) pointed out that the adiabatic gradient in a gas dissociating into ions and electrons will decrease from 0·4, the value corresponding to the perfect gas. After this there have been a large number of investigations of the convective zone in stars with various modifications for the calculation of this adiabatic gradient.

Unsöld (1938) deduced an expression for the adiabatic gradient of a gas, one component of which is being ionised. Since in hot stars the radiation pressure is an appreciable fraction of gas pressure, it favours setting up of early convection. This is so because the radiation effect is to decrease the adiabatic gradient and to increase the actual temperature gradient (Underhill 1949a). So the effect of the radiation field on the adiabatic gradient has also to be considered. Consequently Underhill (1949a) modified Unsöld's one component expression to include the radiation field. Unsöld (1948) gave a general method of calculating the adiabatic gradient of a gas from entropy considerations where several components may be in the process of ionisation. His method is to calculate the entropy of the gaseous mixture as a function of log T and log P_g . The adiabatic gradient is then obtained by numerical differentiation along the loci of constant entropy. Underhill (1949b) pointed out that the entropy due to radiation field is also to be added to the entropy of the gaseous mixture and suggested how Unsöld's method should be modified. Using this method of calculating the adiabatic gradient, Pecker (1953) has constructed many atmospheric models. Although Unsöld's method of calculating the adiabatic gradient from entropy considerations is most general, but it is a bit laborious process. Unsöld (1948) has given a general table of entropy for a gaseous mixture. This table has been widely used so far. If one is to add the correction for radiation also, then one has to add to this able a corresponding table for entropy of radiation for these values of log T and log P_g . Then one has to add the two to get the final table which is to be used for numerical differentiation. It is found that in order to follow this method effectively one would need more points in Unsöld's table to make the differences in the final table small and smooth. To avoid this labour and on the top of this the approximation of numerical differentiation an attempt in the present paper has been made to drive an expression for the adiabatic gradient for a mixture of elements including the effect of radiation field from energy considerations. First an expression of the adiabatic gradient will be derived when only two elements are changing their degree of ionisation and then finally the result will be generalised for a number of elements.

DERIVATION OF THE EXPRESSION

Consider an enclosure of volume V in thermodynamic equilibrium at temperature T containing radiation and N atoms. The various elements present are having the relative abundance v_i by number such that $\Sigma v_i = 1$ and the degree of ionisation x_i . If P_g denotes the gas pressure and P_r the radiation pressure, the total pressure P is given by

$$P = P_r + P_g \tag{2}$$

where

$$P_r = 1/3\ a\ T^4 \tag{3}$$

and

$$P_g = (1 + \bar{x})\ \frac{NkT}{V} \tag{4}$$

Here $\bar{x}$ denotes the mean degree of ionisation defined by,

$$\bar{x} = \Sigma\, v_i\, x_i \tag{5}$$

Differentiating logarithmically equation (4) we get,

$$\frac{dP}{P_g} = \frac{dT}{T} - \frac{dV}{V} + \frac{d\bar{x}}{(1+\bar{x})} \tag{6}$$

The total internal energy of the system is the sum of the kinetic and potential energies of the particles and the radiation energy in the volome. If the energy of radiation per unit volume is u, the interal energy will be Vu. Since $u = a\,T^4$ for radiation in thermodynamic equilibrium at temperature T, the radiation enery in the volume will be aT^4V.

Therefore

$$E = \{\, 1 + \bar{x}\,)\, 3/2\, kT + \Sigma\, v_i\, x_i\, X_i\, \}\, N + V\alpha T^4$$

$$\text{or } dE = dT\, \{3/2\, Nk\, (1+\bar{x}) + 4\, V\alpha T^3\} + \tag{7}$$

$$\Sigma\, v_i\, dx_i\, NkT\, \left\{3/2 + \frac{X}{kT}\right\} + \alpha T^4\, dV \tag{8}$$

Using (3), equation (8) reduces to

$$dE = dT\, \left\{3/2\, Nk\, (1+\bar{x}) + \frac{12\, P_r\, V}{T}\right\} +$$

$$\Sigma v_i\, dx_i\, NkT\, \left\{3/2 + \frac{X_i}{kT}\right\} + 3\, P_r\, dV \tag{9}$$

For an adiabatic change

$$dE + PdV = dQ = 0 \text{ or } \frac{dE}{PV} = -\frac{dV}{V} \tag{10}$$

from equation (6), (9) and (10) finally one gets,

$$\frac{dP_g}{P_g}\left[1 + \frac{4P_r}{P_g}\right] = \frac{dT}{T}\left[5/2 + \frac{16\, P_r}{P_g}\right] + \frac{\Sigma v_i\, dx_i\, (5/2 + X_i/kT)}{(1+\bar{x})} \tag{11}$$

$$+ \frac{4\, (\,P_r\,/P_g\,)\, \Sigma\, v_i\, dx_i}{(1+\bar{x}\,)}$$

Differentiating logarithmically Saha's equation

$$\left(\frac{x_i}{1-x_i}\right)\left(\frac{\bar{x}}{1+\bar{x}}\right)P_g = \text{Const. } T^{5/2}\, e^{-X/kT}$$

one gets,

$$\frac{dx_i}{x_i\,(1-x_i\,)} + \frac{\Sigma\, v_i\, dx_i}{\bar{x}\,(1+\bar{x})} + \frac{d\,P_g}{P_g} = \frac{dT}{T}\left(5/2 + \frac{X_i}{kT}\right) \tag{12}$$

Since all $dx_i = 0$ except for $i = 1$ and 2, by solving equation (12) for dx_1 and dx_2 the values obtained are as follows :

[100]

$$dx_1 = \frac{dT}{T}\,(\alpha\beta)^{-1}\left[x_1(1-x_1)\left(5/2+\frac{\chi_1}{kT}\right)\left\{\beta\,\bar{x}(1+\bar{x})+v_1 x_1(1-x_1)(1-x_2)\right\}\right.$$

$$-\alpha\,x_1(1-x_1)v_2 x_2(1-x_2)\left(5/2+\frac{\chi_2}{kT}\right)\right]-$$

$$\frac{dP_g}{P_g}(\alpha\beta)^{-1}\left[x_1(1-x_1)\bar{x}(1+\bar{x})\left\{\beta-v_2 x_2(1-x_2)\right\}\right] \qquad (13)$$

$$dx_2 = \frac{dT}{T}\left[\beta^{-1}x_2(1-x_2)\left\{\alpha\left(5/2+\frac{\chi_2}{kT}\right)-v_1 x_1(1-x_1)\left(5/2+\frac{\chi_1}{kT}\right)\right\}\right]$$

$$-\frac{dP_g}{P_g}\left[\beta^{-1}x_2(1-x_2)\bar{x}(1+\bar{x})\right] \qquad - \quad (14)$$

where

$$\alpha = \bar{x}(1+\bar{x})+v_1 x_1(1-x_1)$$

and $$\beta = \bar{x}(1+\bar{x})+v_1 x_1(1-x_1)+v_2 x_2(1-x_2).$$

Substituting the above values of dx_1 and dx_2 in equation (11) on simplification it can shown that,

$$\frac{dP}{P_g}\left[1+\frac{\bar{x}\left\{v_1 x_1(1-x_1)\left(5/2+\frac{\chi_1}{kT}\right)+v_2 x_2(1-x_2)\left(5/2+\frac{\chi_2}{kT}\right)\right\}}{2\bar{x}+\bar{x}^2-\overline{x^2}}+\right.$$

$$\left.\frac{4P_r}{P_g}\left\{1+\frac{\bar{x}v_1 x_1(1-x_1)+\bar{x}v_2 x_2(1-x_2)}{2\bar{x}+\bar{x}^2-\overline{x^2}}\right\}\right] =$$

$$\frac{dT}{T}\left[5/2+\frac{v_1 x_1(1-x_1)\left(5/2+\frac{\chi_1}{kT}\right)^2+v_2 x_2(1-x_2)\left(5/2+\frac{\chi_2}{kT}\right)^2}{(1+\bar{x})}-\right.$$

$$\frac{\left\{v_1 x_1(1-x_1)\left(5/2+\frac{\chi_1}{kT}\right)+v_2 x_2(1-x_2)\left(5/2+\frac{\chi_2}{kT}\right)\right\}^2}{(1+\bar{x})(2\bar{x}+\bar{x}^2-\overline{x^2})}+$$

$$\left.\frac{4P_r}{P_g}\left\{4+\frac{\bar{x}v_1 x_1(1-x_1)\left(5/2+\frac{\chi_1}{kT}\right)+\bar{x}v_2 x_2(1-x_2)\left(5/2+\frac{\chi_2}{kT}\right)}{2\bar{x}+\bar{x}^2-\overline{x^2}}\right\}\right],$$

where $\overline{x^2}=\Sigma\,v_i x_i^2$.

Hence $\left(\dfrac{d\log T}{d\log P_g}\right)_{ad.} =$

$$1+\frac{\bar{x}\left\{v_1 x_1(1-x_1)\left(5/2+\frac{\chi_1}{kT}\right)+v_2 x_2(1-x_2)\left(5/2+\frac{\chi_2}{kT}\right)\right\}}{2\bar{x}+\bar{x}^2-\overline{x^2}}+$$

$$\frac{\dfrac{4P_r}{P_g}\left[1+\dfrac{\bar{x}\{v_1\,x_1(1-x_1)+v_2\,x_2(1-x_2)\}}{2\,\bar{x}+\bar{x}^2-\bar{x}^2}\right]}{5/2+\dfrac{v_1\,x_1\left(1-x_1\right)\left(5/2+\dfrac{X_1}{kT}\right)^2+v_2\,x_2\left(1-x_2\right)\left(5/2+\dfrac{X_2}{kT}\right)^2}{(1+\bar{x})}-}$$

$$\dfrac{\left\{v_1\,x_1\left(1-x_1\right)\left(5/2+\dfrac{X_1}{kT}\right)+v_2\,x_2\left(1-x_2\right)\left(5/2+\dfrac{X_2}{kT}\right)\right\}^2}{(1+\bar{x})\,(2\,\bar{x}+\bar{x}^2-\bar{x}^2)}+$$

$$\frac{4\,P_r}{P_g}\left[4+\dfrac{\bar{x}\left\{v_1\,x_1\left(1-x_1\right)\left(5/2+\dfrac{X_1}{kT}\right)+v_2\,x_2\left(1-x_2\right)\left(5/2+\dfrac{X_2}{kT}\right)\right\}}{2\,\bar{x}+\bar{x}^2-\bar{x}^2}\right]$$

This is the expression for the adiabatic gradient when only two elements are changing their degree of ionisation. Generalising the above expression for a number of elements and on simplification the final expression is obtained in the following form.

$$\left(\frac{d\log T}{d\log P_g}\right)_{ad.}=\frac{F_1}{F_2}\tag{15}$$

where $F_1=\left(1+\bar{x}\right)+2\,\dfrac{\bar{x}+\bar{x}^2}{\bar{x}+\bar{x}^2-\bar{x}^2}\,\Sigma\,v_i\,x_i\left(1-x_i\right)\left(5/2+\dfrac{X_i}{kT}\right)$

$$+\frac{4\,P_r}{P_g}\left[\left(1+\bar{x}\right)+2\,\dfrac{\bar{x}+\bar{x}^2}{\bar{x}+\bar{x}^2-\bar{x}^2}\Sigma\,v_i\,x_i\left(1-x_i\right)\right].$$

and $F_2=5/2\left(1+\bar{x}\right)+\Sigma\,v_i\,x_i\left(1-x_i\right)\left(5/2+\dfrac{X_i}{kT}\right)^2-$

$$\dfrac{\left\{\Sigma\,v_i\,x_i(1-x_i)\left(5/2+\dfrac{X_i}{kT}\right)\right\}}{2\bar{x}+\bar{x}^2-\bar{x}^2}+\frac{4\,P_r}{P_g}\left[4\left(1+\bar{x}\right)+\dfrac{\bar{x}+\bar{x}^2\,\Sigma\,v_i\,x_i\,(1-x_i)\left(5/2+\dfrac{X_i}{kT}\right)}{2\,\bar{x}+\bar{x}^2-\bar{x}^2}\right]$$

PARTICULARS CASES

1. *The radiation pressure very small i.e.* $P_r/P_g<<1$.

In this case the equation (15) reduces to

$$\left(\frac{d\log T}{d\log P_g}\right)_{ad.}=\frac{\left(1+\bar{x}\right)+\dfrac{\bar{x}+\bar{x}^2}{2\,\bar{x}+\bar{x}^2-\bar{x}^2}\,\Sigma\,v_i\,x_i\,(1-x_i)\,(5/2+X_i/kT)}{5/2\left(1+\bar{x}\right)+\Sigma\,v_i\,x_i\left(1-x_i\right)\left(5/2+\dfrac{X_i}{kT}\right)^2-\dfrac{[\Sigma v_i\,x_i\,(1-x_i)\,(5/2+X_i/kT)]^2}{2\,\bar{x}+\bar{x}^2-\bar{x}^2}}$$

which is Unsöld's formula (1938).

2. *Radiation pressure not small, and only one element is changing its degree of ionisation,* i.e. all $dx_i=0$ except for $i=1$.

For this the equation (15) becomes

$$\left(\frac{d\log T}{d\log P_g}\right)_{ad.}=\frac{\left(1+\bar{x}v_1\,x_1(1-x_1)\left(5/2+\dfrac{X_1}{kT}\right)\propto^{-1}+\dfrac{4\,P_r}{P_g}\left[1+\bar{x}v_1\,x_1\left(1-x_1\right)\propto^{-1}\right]\right)}{5/2+\bar{x}v_1 x_1\left(1-x_1\right)\left(5/2+\dfrac{X_1}{kT}\right)^2\propto^{-1}+\dfrac{4P_r}{P_g}\left[4+\bar{x}v_1 x_1\left(1-x_1\right)\left(5/2+\dfrac{X_1}{kT}\right)\propto^{-1}\right]}$$

where $\propto$ is defined before.

Defining $B = \nu_1 \left[\dfrac{1 + \bar{x}}{x_1\,(1 - x_1)} + \dfrac{\nu_2}{\bar{x}}\right]^{\pm 1}$

and $\quad A = B\left(5/2 + \dfrac{\chi_1}{kT}\right)$

the above expression becomes

$$\left(\frac{d \log T}{d \log P_g}\right)_{ad.} = \frac{\dfrac{4P_r}{P_g}\Big[\,1 + B\,\Big] + \Big[\,1 + B\,\Big(\,5/2 + \dfrac{\chi_1}{kT}\Big)\Big]}{\dfrac{4P_r}{P_g}\Big[\,4 + A\,\Big] + \Big[\,5/2 + A\Big(5/2 + \dfrac{\chi_1}{kT}\Big)\Big]}$$

This is the expression given by Underhill (1949a).

3. *For the case of nonionisable gas and radiation i.e. all $x_i{}'s = 0$.*

Therefore we have from equation (15),

$$\left(\frac{d \log T}{d \log P_g}\right)_{ad.} = \frac{1 + \dfrac{4P_r}{P_g}}{5/2 + \dfrac{16P_r}{P_g}}$$

This is Chandrasekha's form (1939).

COMPARISON

For certain values of temperature and pressure, the adiabatic gradients calculated by the equation (15) and also obtained from entropy considerations are given in Table 1.

TABLE 1

θ	Log P_e	$\dfrac{P_r}{P_g}$	$\left(\dfrac{d \log T}{d \log P}\right)_{ad.}$	Obtained from
			Formula (15)	Entropy considerations.
0·60	0·864	0·635	0·126	0·129
0·54	1·342	0·372	0·140	0·145
0·50	1·582	0·303	0·178	0·184
0·44	1·860	0·273	0·249	0·252
0·40	2·027	0·275	0·242	0·243
0·34	2·424	0·218	0·164	0·169
0·30	2·769	0·168	0·198	0·202
0·24	3·150	0·174	0·299	0·298
0·20	3·406	0·200	0·301	0·301
0·10	4·706	0·171	0·274	0·279

The values of the adiabatic gradient obtained from entropy consideration are taken from Pecker (1953) paper. Pecker gave the values of $\left(\dfrac{d \log T}{d \log P}\right)_{ad.}$ and equation (15) gives $\left(\dfrac{d \log T}{d \log P_g}\right)_{ad.}$. The relation connecting the two is as follows,

$$\left(\frac{d \log T}{d \log P}\right)_{.} = \frac{1 + P_r/P_g}{1 + 4P_r/P_g \left(\dfrac{d \log T}{d \log P_g}\right)} \left(\frac{d \log T}{d \log P_g}\right)_{ad.} \quad .$$

From the table 1 it can be seen that the values obtained from energy and entropy consideration agree well.

In general it may be seen that at one point *i.e.* for one particular value of temperature, only the elements corresponding to one particular ionisation potential will be in a stage of ionisation and therefore only this group of elements will be effective for our adiabatic gradient calculations. The other elements would not contribute any appreciably. But one has to be looking from physical considerations for the effective group *i.e.* in the case of hydrogen ionisation zone the contribution will be from hydrogen alone and for helium ionisation zone the important part will be played by helium alone. In some cases both of them may play important role. Hence in the Unsöld's formula one has to calculate entropy for all the effective constitutents. The previous workers have considered, simply to avoid the above complications, the hydrogen ionisation zone and helium ionisation zone separately and in some cases the combination of the two elements. But in the present formula one does not have to worry about such separate calculations or physcial considerations. The choice of the effective element is already taken care of by the formula through the ionisation. It may be mentioned that although this general formula includes the whole mixture of elements in the stellar material but it will not change appreciably the physical results obtained by previous workers who considered a reasonable mixture of hydrogen and helium only because the contribution from the elements heavier than helium is very small.

ACKNOWLEDGEMENT

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MIXED MESOMORPHISM—II

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ABSTRACT

Continuing our work further (*Proc. Nat. Acad. Sci., India*, **29A**, **35**, 1960, *ibid.* **29A**, 260, 1960) we have examined binary systems in which both the components are liquid crystals. Although continuous series of mixed liquid crystals are formed over the entire range of concentration, it is observed that there takes place a depression in the transition line when the admixed molecules depart from the criterion of similarity; this can be attributed to the difficulty in packing of the molecules. Slope of the transition line can be measured from either side and the group slope values could be deduced therefrom. These values are found to be comparable with those obtained from the study of the binary mixtures where one component is a non-liquid crystal. This suggests that the specific effect of the terminal groups is operative even in the case of liquid crystalline substances.

Earlier*, we have described the formation of mixed mesomorphism in binary systems where one component is a liquid crystal and another a non-liquid crystal. In these systems, the mixed liquid crystals are formed over a certain range of concentration. Continuing the work further, we have now examined binary systems where both the components are liquid crystals by themselves. A continuous series of mixed liquid crystals are obtained over the entire range of the phase diagrams.

EXPERIMENTAL

Preparation and purification of materials:

p-Acetoxybenzal-p-anisidine and p-acetoxybenzal-p-phenitidine are prepared according to the method described earlier (1).

p-Acetoxybenzal-p-anisidine :

Fine white leaflets from alcohol m. p. 112-119°C. (1)

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* *Proc. Nat. Acad. Sci., India*, **29A**, 35, 1960 ; *ibid*, **29A**, 260, 1960.

p-Acetoxybenzal-p-phenetidine :

Fine white needles from alcohol, m. p. 118·5—137·5°C; Analysis : Found : N = 5·037 %, $C_{17}H_{17}NO_3$; requires N = 4·946 %.

p-Azoxyanisole : is purified by repeated crystallisation from alcohol into fine yellow needles, m. p 118—136°C.

Method of study :

The binary systems are studied by the opticel method.

The following binary systems are investigated :

1. *p*-Azoxyanisole : *p*-acetoxybenzal-*p*-anisidine.

2. *p*-Azoxyanisole : *p*-acetoxybenzal-*p*-phenetidine.

3. *p*-Acetoxybenzal-*p*-phenetidine : *p*-acetoxybenzal-*p*-anisidine

DISCUSSION

Prins (2), Kock (3), Bogojawlensky and winogradov (4), Vorlander and Ost (5) and others have reported the formation of mixed liquid crystals wherein one or both the components are liquid crystals; but they seem to have studied the phenomenon of mixed liquid crystallinity from the point of view of phase rule and its applications. The binary systems investigated here comprise of components both of which are liquid crystals. Unlike the binary systems where one component is a non-liquid crystalline substance in which case the transition curve cuts the melting curve at a certain point either to the right or to the left of the eutectic point (6) bounding the mixed liquid crystalline region in a definite area, a continuous series of mixed liquid crystals throughout the whole region of the phase diagrams is obtained in these binary systems. Bogojawlensky and Winogradov (4) have repoted that in the case of isomorphous mixtures the transition lines obtained are straight lines, but it has been shown by Dave and Dewar (7) that the transition lines are not invariably straight and that they may be curved to more or less extent. The above mentioned binary systems are similar to those studied by Bogojawlensky and Winogradov.

A reference to diagrams clearly shows that a depression in the transition lines is observed in the first two systems (figs. 1 and 2) whereas the transition line in the

p-Azoxyanisole : b-Acetoxybenzal-p-anisidine.

Fig. 1

p-Azoxyanisole: p-Acetoxybenzal-p-phenetidine.
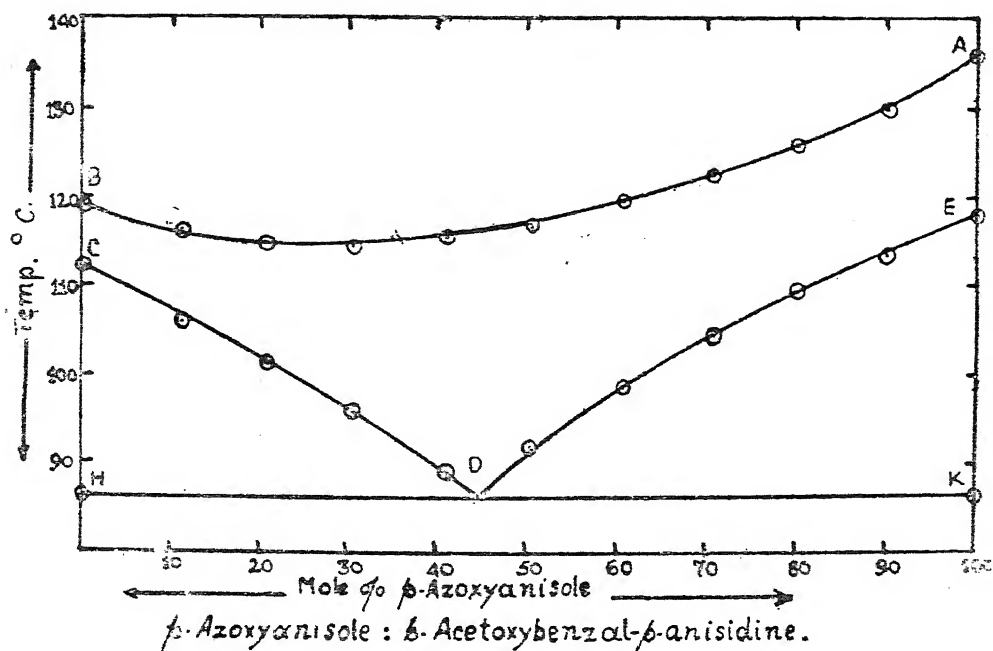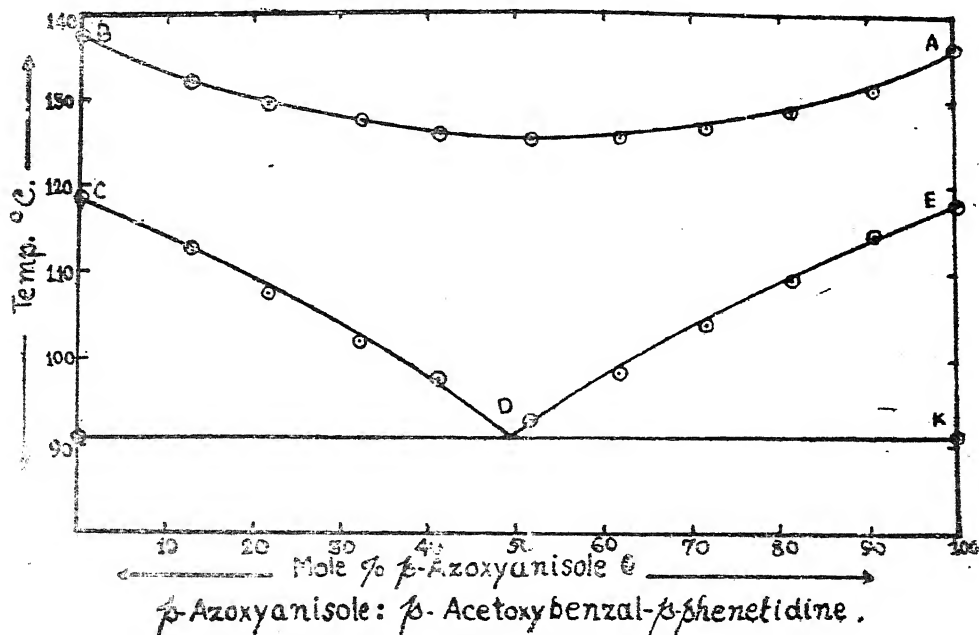
Fig. 2

case of the third system (fig. 3) where both the compenents are liquid crystalline Schiff's bases, is almost straight. The Schiff's bases comprising the system No. 3 possess the same structure, the only difference being of the different terminal groups. The behaviour of the transition line in this system represents an ideal behaviour of mixed liquid crystals ; with the components having the same structure there should be no difficulty in the packing of the molecules together. This should, therefore, indicate that the transition lines will be straight obeying ideally the law of mixtures only when the two admixed molecules are structurally the same.
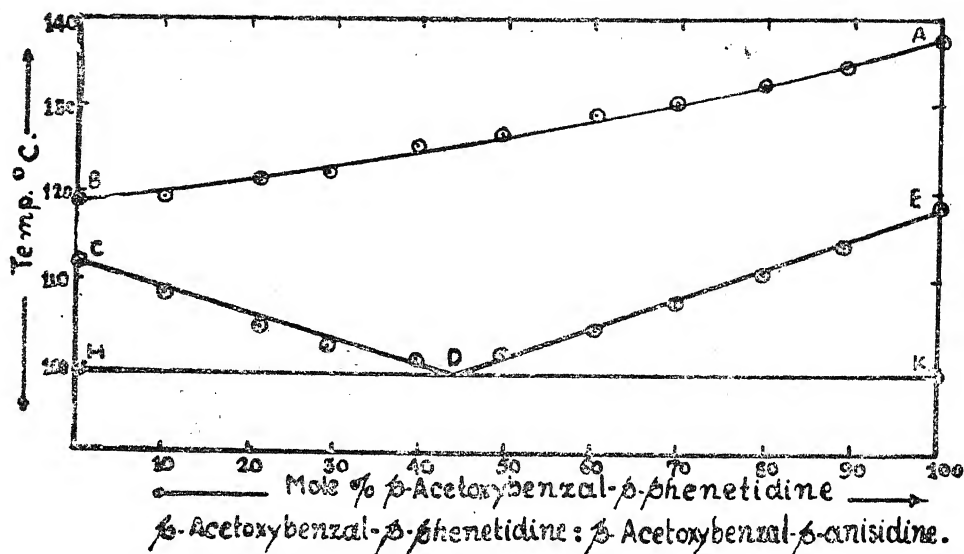
Fig. 3

Dave and Dewar (7) who studied a number of binary systems wherein one component was a liquid crystal and another a non-liquid crystal, have attributed the tendency of the non-liquid crystalline component towards mixed liquid crystal formation in terms of group slopes deduced from the slopes of the transition lines of the systems. These values of the group slopes have been shown to be dependent upon the terminal polar groups present in the non-liquid crystalline component. Dave and Lohar (1) similarly deduced group slopes from the initial slopes of the transition lines of the binary systems investigated by them, for OCH_3, $O.CO.CH_3$, $OC_2 H_5$ and other groups. An attempt is made here to make such a deduction of initial slopes of the transition lines and group slope values for the terminal groups in the case of the binary systems where both the components are liquid crystalline substances by themselves but the transition lines show a slight depression which can be attributed to the difficulty in packing of the molecules due to difference in structure (figs. 1 and 2) (cf. 3, 6). As these systems comprise of components both of which are liquid crystalline substances, evidently, the initial slopes of the transition lines on the right hand side of the diagrams are the slopes for the second component while on the left

hand side are the slopes for the first component. These values for the slopes of the transition lines are given in table 1.

TABLE 1

Substance	System No.	Slope of the Transition line ($^{\circ}$C/mole %) $\times$ 10
p-Azoxyanisole	1	3·8
p-Azoxyanisole	2	4·2
p-Acetoxybenzal-p-anisidine	1	5·5
p-Acetoxybenzal-p-phenitidine	2	4·5

Values for the group slopes for the terminal groups have been deduced from these on the basis of the additivity principle (1 and 7). The group slope values for OCH_3, $O.CO.CH_3$ and OC_2H_5 are given below in table 2 and it is observed that these compare well with the values obtained for these groups from the binary systems in which one component is a non-liquid crystalline substance (1,7).

TABLE 2

End Group	Group Slope (One component non-liquid crystal) (1,7)	Group Slope (Both components liquid crystals)
.OCH_3	2·0	2·0
$O.CO.CH_3$	3·05	3·5
OC_2H_5	1·0	1·0

This shows that the group effects are specific and operate even when the substances are liquid crystals by themselves. This should substantiate the view that the groups and subsequently the polarities are responsible for liquid crystalline tendency of a substance. However, it should be mentioned here, that group slopes from the initial slope of the transition line in the case of system No. 3, can hardly be deduced as the transition line shows no depression. This shows that such deductions in such binary systems consisting of both liquid crystalline substances can only be made where the components depart from the criterion of similarity.

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